

Preparation of Porous YSZ Using SiO₂ as Pore FormerMoon-Jin Hwang, Youngmin Chung,[†] Jeong-Hun Ju,[†] Yu-Rim Bak,[†] Youngil Lee,[†] Han Mo Jeong,[†] Ki-Whan Chi,[†] Sang Youn Park,[†] and Kwang-Sun Ryu^{†,*}

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The porous yttria stabilized zirconia (YSZ) has attracted much attention in a various field of scientific and industrial applications, such as ceramic membrane filter, gas separator, oxygen generator, sensor, thermal insulator, catalyst support, and anode material of solid oxide fuel cell. The macroporous YSZ has been typically prepared by using pyrolyzable or non-pyrolyzable pore formers. Carbon, organic polymer, starch, graphite, polymethacrylate, and polystyrene as pyrolyzable pore formers and Ni/NiO and ZnO as nonpyrolyzable pore formers were used to prepare porous YSZ.¹⁻⁵

A lot of reports have demonstrated that spherical SiO₂ particles produce a simple and reliable method to fabricate hollow ZrO₂ powder and porous ZrO₂ membranes.^{6,7} The preparation and characteristics of porous YSZ prepared using SiO₂ as a pore former or sacrificial core have not been reported until now. In this study, porous YSZ with homogeneous and controllable pore morphology was prepared using a spherical SiO₂ as a pore former. YSZ precursor was absorbed and polymerized on the surface of the SiO₂ at mild temperature without the use of a surfactant, catalyst, support material, and high pressure. We investigated the structural properties of the porous YSZ prepared using the SiO₂ spheres.

Tetraethylorthosilicate (TEOS, 98%) and Y(NO₃)₃·6H₂O were purchased from Sigma-Aldrich Chemicals Ltd. and ZrOCl₂·8H₂O was obtained from Junsei Chemical Co., Ltd. (Japan). Ethanol (99.5%), NH₄OH (25 ~ 28%), anhydrous citric acid, and NaOH were supplied by Dae Jung Chemical Co. (Korea). Distilled water was used in this experimental. Silicon dioxide spheres were fabricated according to previously reported methods.⁸ A 250 mL ethanol solution containing 23 mL TEOS and a 250 mL ethanol solution containing 42 mL NH₄OH and 153 mL distilled water were blended with vigorous stirring for 48 hrs. The molar concentrations of TEOS, NH₄OH, and H₂O in the blending solution were 0.2, 0.6, and 17 M, respectively. A slightly milky white suspension of the colloidal SiO₂ was observed after 1 min of reaction time at room temperature. Silicon dioxide was centrifuged at 3,000 rpm for 20 min and washed with ethanol and water several times. The SiO₂ was prepared by drying the collected SiO₂ particles at 100 °C and heating at 600 °C for 6 hrs. The SiO₂/YSZ composite was fabricated from the mixture of the dispersion solution of SiO₂ and the YSZ precursor solution. The 1 g of SiO₂ was added to 100 mL ethanol and treated under ultrasonic waves for 2 hrs to prepare the SiO₂ dispersion solution. The 1.3 g of ZrOCl₂·8H₂O and the 0.27 g of Y(NO₃)₃·6H₂O were dissolved in 100 mL ethanol/water (1:1

volume ratio) and then 0.02 g citric acid was added as a complexing agent to obtain the YSZ precursor for the YSZ containing 8 mol % Y₂O₃ and 92 mol % ZrO₂. The dispersion solution of SiO₂ particles and the YSZ precursor solution were mixed and heated at 80 °C until the solutions volume was about 10 mL. The 10 mL solution was placed in the ultrasonic bath and sonicated until all of the solvent was vaporized, leaving insoluble YSZ precursor gel on the SiO₂. The SiO₂/YSZ precursor composite was exposed to air for 24 hrs to stabilize its structure. The SiO₂/YSZ precursor was washed with 25 mL ethanol under ultrasonic waves for 5 min in order to eliminate impurities. The SiO₂/YSZ precursor was heated at 550 °C for 6 hrs in air to form the SiO₂/YSZ composite. Porous YSZ was obtained by leaching the SiO₂ from the SiO₂/YSZ with NaOH solution. The SiO₂/YSZ was treated in 1 M NaOH aqueous solution for two days at room temperature. The SiO₂/YSZ was treated again in fresh 1 M NaOH aqueous solution to ensure the complete removal of SiO₂. Porous YSZ was washed five times with distilled water. Porous YSZ was collected without centrifugation after washing.

The crystalline phases of the samples were analyzed with X-ray diffraction analysis with a Rigaku ultra-X (Cu K_α radiation, 40 kV, 120 mA). The morphologies of the SiO₂, SiO₂/YSZ composite and porous YSZ samples were measured using scanning electron microscopy (SEM, Supra 40 - Carl Zeiss Co., Ltd). The elemental analysis of the porous YSZ was performed using energy dispersive X-ray spectroscopy (EDS). The pore characteristics of the SiO₂, SiO₂/YSZ, and porous YSZ were measured using the Brunauer-Emmett-Teller method (BET,

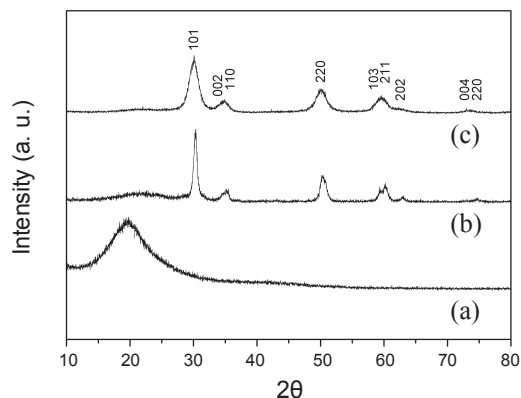


Figure 1. XRD patterns of (a) the SiO₂, (b) the SiO₂/YSZ composite, and (c) the porous YSZ.

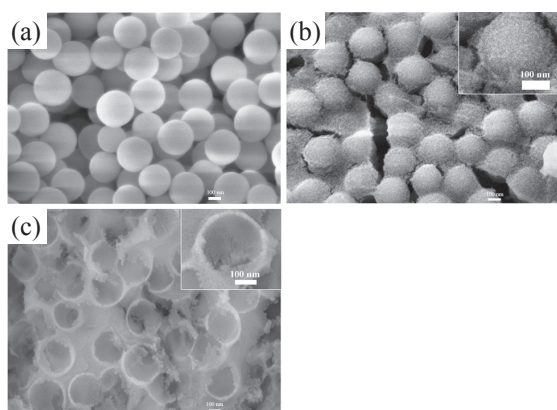


Figure 2. SEM images of (a) the SiO₂, (b) the SiO₂/YSZ composite, and (c) the porous YSZ (scale bar is 100 nm).

nanoPOROSITY-XQ, Mirae Scientific Instruments Co., Korea).

Figure 1 shows the XRD patterns of the SiO₂, the SiO₂/YSZ composite, and the porous YSZ. The XRD patterns of the amorphous SiO₂ showed a broad peak, centered at $2\theta = 21.34^\circ$, in the range of $15 \sim 25^\circ$ (Fig. 1(a)). The XRD patterns of the SiO₂/YSZ showed broad peaks due to small crystallites and unclear grain boundaries of the tetragonal YSZ with the space group P4₂/nmc formed on the SiO₂ (Fig. 1(b)). In Fig. 1(c), more weak and broad peaks of the porous YSZ were observed after removal of SiO₂ from the SiO₂/YSZ composite in an NH₄OH aqueous solution. The weak broad peaks at $20 \sim 25^\circ$ were estimated to be carbon peaks originating from citric acid. From the calculation results using the Scherrer equation, the crystal sizes for the diffraction peak, corresponding to the 101 plane of YSZ in Fig. 1(b) and Fig. 1(c), were 14.1 nm and 4.8 nm, respectively. From the decrease of the crystal size estimated by the 101 peak broadening of the porous YSZ, it is suggested that the new cracks or voids on the surface and the inner place of the porous YSZ shell were formed during the SiO₂ removal process.

Figure 2 shows the SEM images of the SiO₂, the SiO₂/YSZ composite, and the porous YSZ. Mono-dispersed SiO₂ spheres with a mean diameter of 284 nm were obtained by hydrolysis of TEOS in ethanol containing H₂O and NH₄OH as a catalyst to control the shape and size of the SiO₂ core, as shown in Fig. 2(a).⁹ After heating of the SiO₂/YSZ precursor, the formation of cracks or voids below 150 nm in the space of the adjacent SiO₂/YSZ particles was observed in Fig. 2(b) and these cracks or voids were caused by the vibration of the SiO₂/YSZ particles during washing, sonication, and/or heating. The leaching of the SiO₂ in the SiO₂/YSZ composite resulted in the formation of porous YSZ, as shown in Fig. 2(c), with about 20 nm of the shell thickness and about 282 nm of the inner pore size. It could be known that the size of the SiO₂ produces reliable pore size of the porous YSZ. The inset of Fig. 2(c) shows definitely that the small voids were formed in the porous YSZ.

The elemental contents of C, O, Na, Si, Cl, Y, and Zr in the porous YSZ were analyzed with SEM/EDS and the analysis data are listed in Table 1. Chlorine ions were easily removed during the washing and heating process, while the sodium ions were effectively removed during the washing process. Based on the weight percents of Y and Zr, the mol % of yttria in the

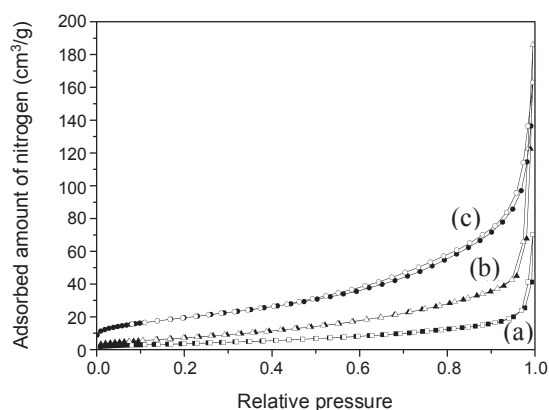


Figure 3. The N₂ adsorption-desorption isotherms of (a) the SiO₂, (b) the SiO₂/YSZ composite, and (c) the porous YSZ.

Table 1. EDS analysis data of porous YSZ

Sample	Weight %							Total
	C	O	Na	Si	Cl	Y	Zr	
Porous YSZ	6.74	28.06	0.42	1.39	0.00	9.27	54.20	100

porous YSZ was calculated to be about 7.5 mol %.

Fig. 3 shows the pore characteristics of the SiO₂, the SiO₂/YSZ composite, and the porous YSZ. In Fig. 3, the filled symbol solid line and the open symbol solid line indicate the N₂ adsorption and desorption branches, respectively. The specific surface areas of the SiO₂, the SiO₂/YSZ composite, and the porous YSZ were 13.73, 26.69, and 71.39 m²/g, respectively. The specific surface area of the SiO₂/YSZ composite was increased to 26.69 m²/g by the YSZ coating on the SiO₂ and the formation of new cracks between the SiO₂/YSZ composites. The specific surface area of the porous YSZ was increased to 71.39 m²/g after the removal of SiO₂ in the SiO₂/YSZ composite. From the results of Fig. 1 and Fig. 2, it could be known that the decreased YSZ crystal size and the formation of small voids in the porous YSZ resulted in the remarkable increment of surface area.

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