Fabrication of zirconium oxide solid electrolytes with ordered porous structures by using micro stereolithography†

KIRIHARA Soshu * and TASAKI Satoko *

KEY WORDS: (Solid electrolytes) (Zirconium oxide) (Ordered porous structures) (Micro stereolithography)

1. Introduction

Zirconium oxide solid electrolytes with ordered porous structures were successfully fabricated by using novel micro stereolithography with computer aided design and manufacture processes. Micrometer order zirconia ceramic lattices with coordination number 4 were propagated spatially to realize high porosities from 60 to 80 percent. In these fabrication processes, nanometer sized zirconia particles were dispersed in photo sensitive resins to obtain thixotropic slurries. The paste was spread on a glass substrate by using a mechanic at knife edge movement, and an ultra violet micro pattern was exposed on the surface to create a cross sectional solid layer. After the layer stacking processes [1-3], a micrometer order structure of the resin and ceramic composite was obtained. The formed composite precursor was dewaxed and sintered at high temperatures in an air atmosphere, and the fine ceramic lattices with high density were created.

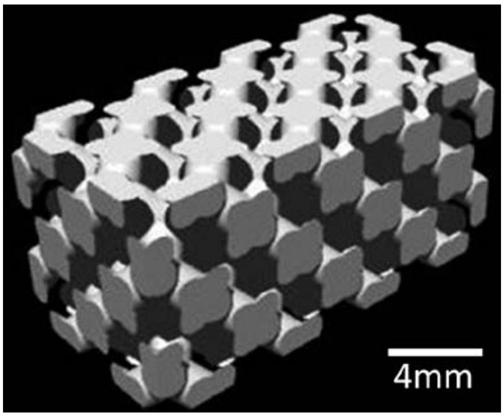

Fig. 1 A computer graphic model of a solid electrolytes with ordered porous structure. A ceramic lattice distributes in air space to create periodic arrangements of opened paths.

2. Experimental Procedure

The zirconia lattice model with the coordination number 4 was created by the computer graphic application (Toyota Keram, Think Design) as shown in **Fig. 1.** The crystal lattice model of 3×3×0.37 mm in size included the arranged rods of ϕ100×150 mm in dimension. The volume ratio of the lattice was 33.3 %. The real ceramic lattice model was fabricated automatically by using the stereolithographic machine (D-MEC, SI-C1000). **Figure 2** shows a schematic illustration of the fabrication system. The designed model was converted into a rapid prototyping format of the stereolithography files and sliced into thin sections. The zirconia particles of 100 nm in average diameter were dispersed into photo sensitive acrylic liquid resin at 30 % in volume content. The mixed slurry was squeezed on a working stage from a dispenser nozzle. This material paste was spread uniformly by a moving knife edge. The layer thickness was controlled to 5 μm. An ultra violet layer of 405 nm in wavelength was exposed on the resin surface according to the computer aided operations. Two dimensional solid patterns were obtained by light induced photo polymerization. The high resolutions in these micro patterns had been achieved by using a digital micro mirror device. In this optical device, square aluminum mirrors of 14 μm in edge length were closely assembled with 1024×768 in number. Each micro mirror can be tilted independently, and cross sectional patterns were dynamically exposed through the objective lens as bitmap images of 2 μm in space resolution. After the stacking and joining these layers through photo solidifications, the

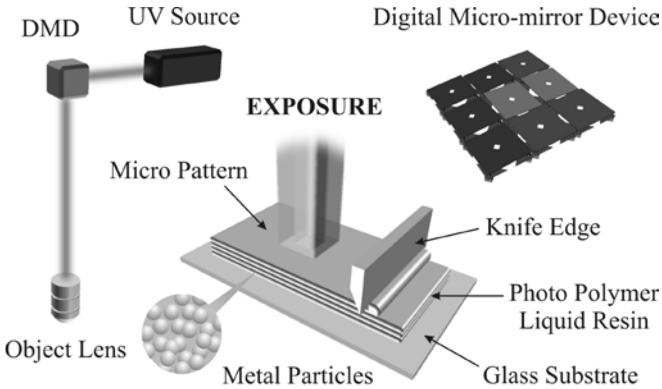

Fig. 2 A schematically illustrated micro stereolithography system. Acrylic resin lattices including zirconia nano-sized particles were processed through solidified layers stacking.

† Received on 30 September 2010
* JWRI, Osaka University, Ibaraki, Japan

Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

periodic arrangements of micro dielectric tablets were btained. After the dewaxing process of the zirconia dispersed resin precursor at 600 ºC for 2 hs with a heating rate of 1 ºC/min, the sample was sintered at 1500 ºC for 2hs with a heating rate of 8 ºC/min. Relative densities of these sintered samples were measured by using the Archimedes method. Part accuracy of the ceramic lattice arrangement in the metal matrix was measured by using the digital optical microscope (Keyence, VHX-200). And, microstructures of ceramic phases were closely observed by using the scanning electron microscope (JEOL, JSM-6060).

3. Results and Discussion

The stereolithographic models of the acryl lattice pattern with the zirconia nano particles were successfully fabricated. The spatial resolution was measured as 0.5 % in size. The nanometer sized zirconia particles were dispersed uniformly in the acrylic resin matrix as shown in **Fig. 3**. Through the heat treatments of the precursors, the micrometer order zirconia lattices including the air gaps were formed exactly as shown in **Fig. 4**. By the optical and scanning microscopic observations, the deformation and cracking were not observed. Linear shrinkages for the horizontal and vertical axis were different at 2 % approximately. Uniform shrinkage will be obtained through the optimizations in the model design considering the gravity effect. The relative density reached 98.5 %. Dense zirconia microstructure was formed, and the average grain size was approximately 2 µm.

4. Conclusions

We have fabricated three dimensional solid electrolytes of zirconia lattices successfully by using stereolithography. These ceramic lattices with coordination number 4 could realize ordered porous structures. The fabricated ceramic structures with high porosities and wide surface areas are expected to be applied to novel electrodes in solid fuel cells.

5. Acknowledgments

This study was supported by Priority Assistance for the Formation of Worldwide Renowned Centers of Research - The Global COE Program (Project: Center of Excellence for Advanced Structural and Functional Materials Design) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

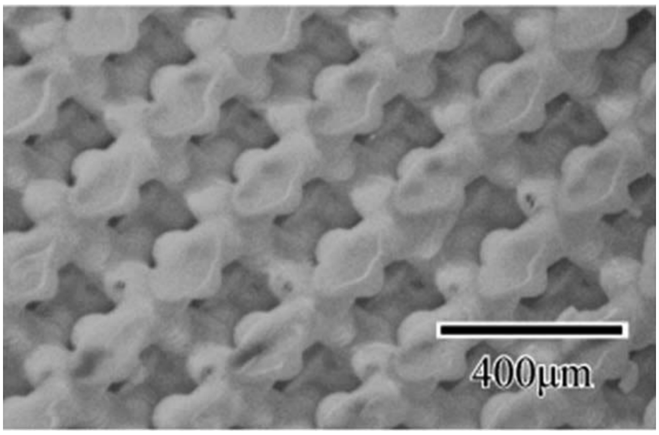

Fig. 3 The nanometer sized particles of the zirconium oxide ceramics dispersing in the acrylic resin lattices fabricated by using the micro stereolithography process.

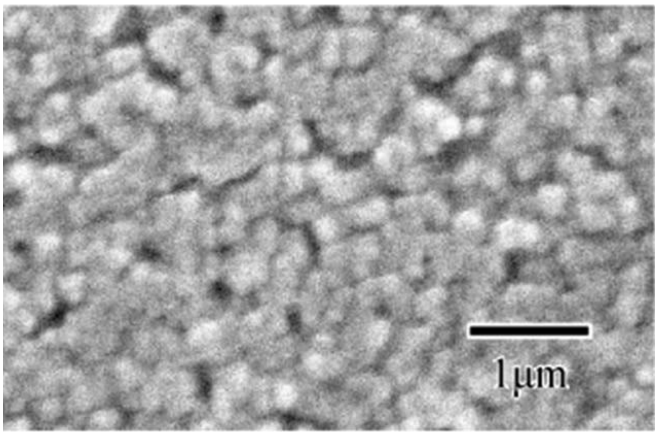

Fig. 4 The sintered zirconium oxide lattices with the ordered porous structures. The lattice coordination number is 4. The opened air paths were arranged periodically.

References

[1] C. Kai and L. Fai: *Rapid Prototyping*, Singapore John Wiley and Sons, (1997).
[2] A. Pique, A. Holmes and D. Dimos: Materials Research Society Symposium Proceedings, (2003), pp.758-764.
[3] S. Kanehira, S. Kirihara and Y. Miyamoto, Journal of the American Ceramic Society, 88 (2005), pp.461-1464.
[4] S. Kirihara and Y. Miyamoto, The International Journal of Applied Ceramic Technology, 6 (2009), pp.41-44.