Three Dimensional Printing of Solid Electrolyte Dendrites with Ordered Porous Structures for Fuel Cell Miniaturizations†

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Abstract

Solid electrolyte dendrites of yttria stabilized zirconia with spatially ordered porous structures were successfully fabricated for fuel cell miniaturizations by using a micro patterning stereolithography and three dimensional printing. Micrometer order ceramic lattices with the coordination numbers 4, 6, 8 and 12 were propagated spatially in computer graphic space. Aspect ratios of the lattice diameters and lengths were designed between 1.0 and 2.0 to value the porosities in higher levels from 50 to 80 %. On the fabrication process, nanometer sized yttria stabilized zirconia were dispersed in photo sensitive liquid resins at 30 % in volume fraction to obtain thixotropic slurries. The paste material was spread on a glass substrate with 10 μm layer thickness by using mechanical knife edge movements, and an ultra violet micro pattern was exposed on the surface to create a cross sectional solid layer with 2 μm in part accuracy. After the layer stacking process, the ceramic dispersed resin lattices of 100 μm in diameter were obtained exactly. These composite precursors were dewaxed and sintered at 600 and 1500 ℃ in an air atmosphere, respectively, and fine ceramic lattices of 98 % in relative density were created. Gaseous fluid profiles and pressure distributions in the formed ceramic lattices with the various coordination numbers and porosity percents were visualized and analyzed by using a finite element method. The fabricated solid electrolytes with the extremely high porosities and wide surface areas are expected to be applied to novel electrodes in compact fuel cells. The smart processing of the solid electrolytes by utilizing computer aided design, manufacturing and evaluation methods will be demonstrated.

KEY WORDS: (Solid Oxide Fuel Cell), (Ceramic Electrolyte Dendrite), (Yttria Stabilized Zirconia), (Micro Pattering Stereolithography), (Computer Aided Design, Manufacturing and Evaluation)

1. Introduction

Solid oxide fuel cells (SOFCs) are investigated as novel generation systems of electric power with high efficiencies in energy conversion circulations. Yttria stabilized zirconia (YSZ) with high ion conductivities for incident oxygen is a widely adopted material for solid electrolyte anodes as SOFC components [1-5]. Recently, porous network structures were introduced into YSZ electrodes in micrometer or nanometer sizes to increase surface areas of reaction interfaces and gap volumes of stream paths [6-8]. In this investigation, solid electrolyte dendrites composed of YSZ spatial lattice structures with various coordination numbers were fabricated by using micro patterning stereolithography and powder sintering techniques. In the dendrite structure, stress distributions and fluid flows were simulated and visualized by using finite element methods. The automatically manufactures and evaluations have been established to create micro ceramics components in our investigation group [9-17].

2. Experimental

The solid electrolyte dendrites with spatial lattice structures were designed by using a computer graphic application (Think Design: Toyota Caelum, Japan) as shown in **Figure 1**. These surface areas of reaction interfaces and the gap volume of stream paths were calculated geometrically for the dendrite lattice with four coordination numbers as shown in **Figure 2**. The dendrite lattices of 1.16 in aspect ratio can be considered to exhibit the higher reaction efficiencies and gas transmittances according to the Nernst equation. In the optimized dendrite structure, the diameter and length of YSZ rods were decided 92 and 107 μm, respectively. The lattice constant was 250 μm. The graphic data was converted into a stereolithographic file format through polyhedral approximations. The solid model was sliced into the cross sectional numerical data sets to input the stereolithographic equipment (D-MEC: SI-C1000, Japan). Photo sensitive acrylic resin dispersed with YSZ ceramic

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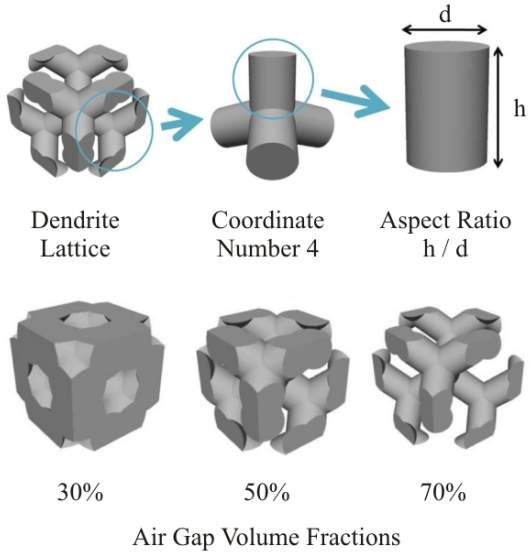

Fig. 1 Computer graphics of lattice distributions of dendrite structures with coordination number four. Air gap volume fractions are changed with aspect ratios.

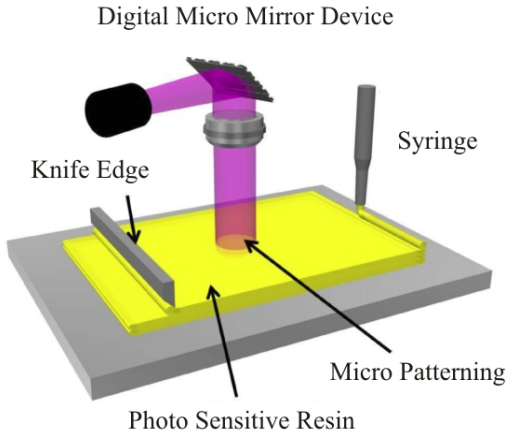

Fig. 2 A schematic illustration of micro patterning stereolithography. Fine images are exposed by using a digital micro mirror device on a photo sensitive resin.

particles of 60 and 100 nm in first and second diameters at 30 volume % were fed over a substrate from a dispenser nozzle. The highly viscous resin paste was fed with controlled air pressure, and spread uniformly by a mechanical knife edge. The thickness of each layer was controlled to 10 μm. The cross sectional pattern was formed through illuminating a visible laser of 405 nm in wavelength on the resin surface. The high resolution image could be achieved by applying a digital micro mirror device (DMD) and an objective optical lens. **Figure 3** shows a schematic illustration of the micro patterning stereo- lithography system. The DMD is an optical element assembled by micro mirrors of 14 μm in edge length. The tilting of each tiny mirror can be controlled according to the cross sectional data transferred from a computer. The solid micro structures were built by stacking these patterns layer by layer. In order to avoid deformation and cracking during dewaxing, careful investigation for the heat treatment processes was required. The formed precursors with dendrite structures were heated at various temperatures from 100 to 600 °C while the heating rate was 1.0 °C /min. The dewaxing process was observed in respect to the weight and color changes. The YSZ particles could be sintered at 1500 °C for 2 hs. The heating rate was 8.0 °C/min. The density of the sintered sample was measured by using the Archimedes method. The ceramic microstructures were observed by a digital optical microscope and scanning electron microscopy. In the lattice dendrites, fluid flow velocities and pressure stress distributions were simulated and visualized by a finite volume method (FVM) application (Ansys: Cybernet Systems, Japan).

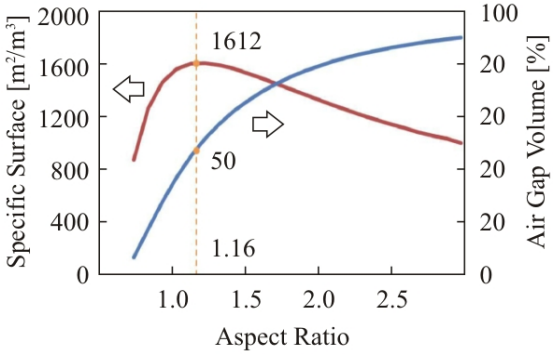

Fig. 3 Optimization of the aspect ratio to obtain the widest specific surface and higher air gap volume. The aspect ratio was decided as 1.16 for designing.

3. Results and Discussion

The dendrite lattice structures composed of the YSZ dispersed acrylic resins were processed exactly by using the stereolithography as shown in **Figure 4**. The spatial resolution was approximately 1.0 %. The microstructure of the composite lattice is shown in **Figure 5**. The nanometer sized YSZ particles were dispersed homogeneously in the acrylic matrix. **Figure 6** shows the sintered solid electrolyte dendrite with the YSZ micro lattice structure. Deformation and cracking were not observed. The linear shrinkages on the both horizontal and vertical axis were 32 %. The volume fraction of the air gaps was 50 % by the open paths. In the previous investigations, the porous electrodes were formed by sintering the YSZ surly with polystyrene particles dispersion. Therefore, it is difficult to realize the perfect opened pores structures with the higher porosity over 40 % in volume fraction. **Figure 7** shows the dense micro-structure of the YSZ lattice. The average grain size was approximately 4 μm. The relative density reached 95 %. Micrometer sized cracks or pores were not observed. The obtained dense YSZ lattice structure will exhibit higher performances in mechanical properties as the porous electrodes of the solid electrolyte dendrites.

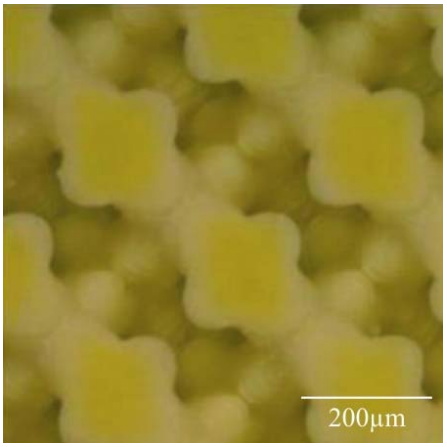

Fig. 4 Acrylic dendrite lattices with YSZ particles dispersion fabricated by using the stereolithography.

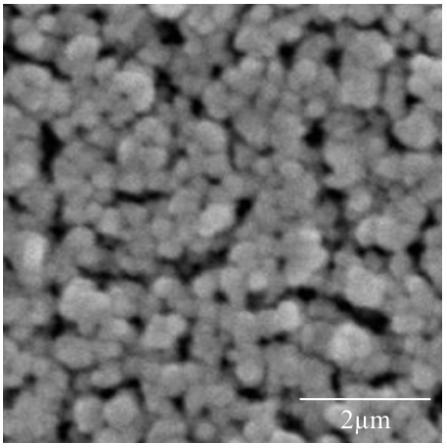

Fig. 5 The nanometer sized YSZ particles in the acryl dendrite lattice. The volume fraction is 30 %.

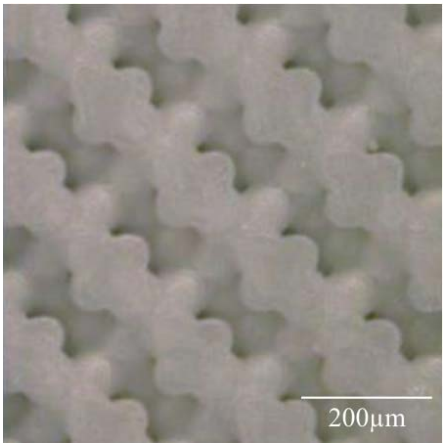

Fig. 6 The sintered dendrite lattices of YSZ solid electrolyte. The part accuracy of the lattice is 2 μm.

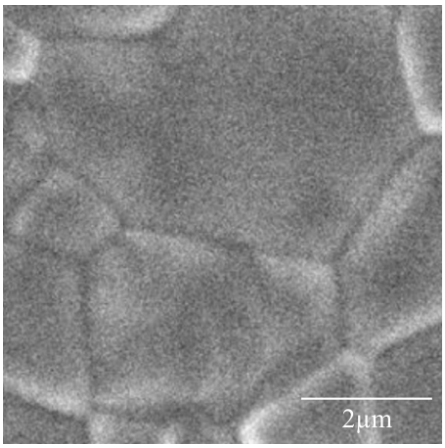

Fig. 7 The microstructure of YSZ micro lattice in the dendrite structure. The average grain size is 4μm.

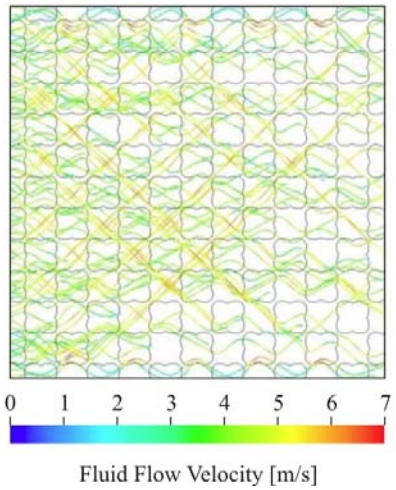

Fig. 8 A distribution of fluid flow velocities in the dendrite lattice structure simulated by FVM method.

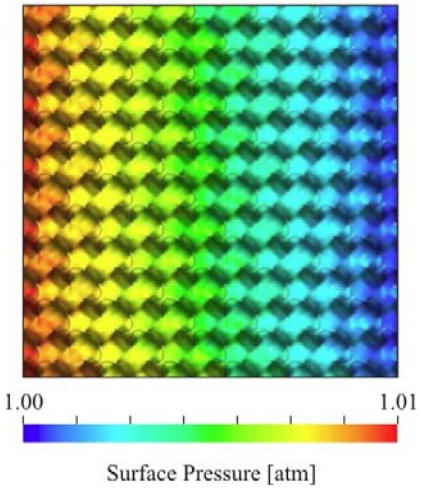

Fig. 9 The distribution of the surface pressure on the ceramics lattice of dendrite structure.

The fluid flow velocities were visualized by using the FVM method as shown in **Figure 8**. Continuously curved lines indicate the fluid distributions along the vector directions of flow velocities. All air paths were opened for outsides and connected with each other in the YSZ dendrite lattice structures. The fluid flows can transmit in one direction smoothly. The pressure stress distributions in the dendrite were visualized as shown in **Figure 9**. The fluid pressures were gradually distributed for flow direction, and localization of the stress was not observed. The fabricated solid electrolyte dendrites with YSZ lattice structures can be considered to have higher performances as ceramic electrodes in future SOFCs.

4. Conclusions

We have fabricated solid electrolyte dendrites with yttria stabilized zirconia lattices for anode electrodes of solid oxide fuel cells. Acryl precursors including ceramic particles were formed successfully by using micro patterning stereolithography process and equipment. By careful optimization of process parameters in dewaxing and sintering, we have succeeded in fabricating dense ceramic micro components. These solid electrolyte dendrites with opened air path networks exhibited effective transmission properties of fluid flows. These novel ceramic electrodes have potentials to contribute to developments of compact fuel cells.

5. Acknowledgments

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