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Co-firing sintering properties on electrolyte, anode support and anode functional layer of electrolyte for solid oxide fuel cells

Seung-Hwan Lee^a, Woo Chang Song^b, Yoo-Jung Choi^c and Jung-Rag Yoon^{c,*}

^aInstitute for Research in Electronics and Applied Physics, University of Maryland, College Park, Maryland 20742, USA ^bDepartment of Electrical Engineering, Kangwon National University, Samcheok 24341, Korea ^cR&D Center, Samwha Capacitor, youngin, Korea

We investigated the various mixing conditions (powder/binder, solvent/binder and viscosity) and sintering conditions (1290 °C, 1310 °C, 1350 °C and 1390 °C) of anode support, anode functional layer, and electrolyte using tape casting method to fabricate the laminated unit cell for the use of solid oxide fuel cells. From various experiments, we obtained the optimize mixing and sintering conditions for superior solid oxide fuel cells. From microstructures of components, we prepared the uniform anode functional layer, electrolyte, anode support without bending, interfacial delamination and crack. Ultimately, we successfully fabricated cost-effective laminated unit cell. We can conclude that these results will enable us to fabricate high-grade laminated solid oxide fuel cells by appropriate method for mass production.

Key words: Anode Functional Layer, Electrolyte, Co-firing, Solid Oxide Fuel Cell.

Introduction

A fuel cell is a type of energy conversion system that converts chemical energy of a hydrogen fuel to electrical energy. In contrast with solar cell and wind power generation, fuel cell is able to consistently generate electric power under sufficient gas supply regardless of the external environment. Among the various fuel cell types, the solid oxide fuel cell (SOFC) composed of the ion conductive electrolyte and electrode using ceramic materials can convert chemical energy to electrical and thermal energy by the electrochemical reaction between fuel and oxygen gas in the temperature range from 600 to 1000 °C [1-3]. It also shows the best energy conversion efficiency in the fuel cell. Therefore, the SOFC can be regarded as a future generator system. The unit cell of SOFC is divided into tube and flat type. Moreover, the unit cell with equivalent structure was also classified into three types according to the support application method: anode-supported cell (ASC), cathode-supported cell (CSC), and electrolytesupported cell (ESC) [4, 5]. Recently, in order to increase the density of electrolyte per unit volume, the development of unit cell by tape casting which enable to adopt a thin film type electrolyte support and laminated using co-firing has been extensively studied. Among them, the tape casting method has been extensively adopted to industry because it can fabricate a large area sintered ceramic at low cost with

maintaining high quality. The uniform sintered ceramic devoid of defect can be obtained by a fabrication of uniform and high packing-density green sheet. To satisfy this, the study of appropriate viscosity, dispersion, and drying conditions for tape casting is necessary [6, 7]. In particular, the solid content and laminating pressure control of slurry were studied to optimaize the shrinkage under sintering process. When the green sheets with different materials were laminated and sintered, the flexure, delamination, and crack were generated, because of the sintering temperature and shrinkage of each material. Therefore, the optimization of the slurry, dispersant, and organic additives is necessary, to obtain the desired structure and properties [8-10]. In this paper, we fabricate the unit cell of laminated SOFC with co-firing process and investigate the mixing ratio and sintering conditions of anode support, anode functional layer, and electrolyte.

Experiments

6Yb4ScSZ powder ((Yb₂O₃)_{0.06}(Sc₂O₃)_{0.04}(ZrO₂)_{0.9}, Kceracell, Korea) with the D50 pore size of 0.67 μ m and a specific surface area of 11.2 m²/g was used as the electrolyte powder. NiO-6Yb4ScSZ (57 : 43 wt%) with D50 pore size of 0.58 im and specific surface area of 4.52 m²/g was used as AFL powder. NiO-3YSZ (55 : 45 wt%) was used as the anode support powder and the 30 vol% of activatied carbon was added for the pore forming to fabricate the porous anode. The B74001 (Ferro, USA), M1201 (Ferro, USA) and the toluene/ethanol (25 : 75 wt.%) were used as a binder and dispersant and solvent, respectively. The powder,

^{*}Corresponding author:

Fax: +82-031-332-6441

E-mail: yoonjungrag@samwha.com

 Table 1. Basic design of unit cell with Electrolyte, AFL and Anode support.

Layer	Function	Material	Thickness
1	Electrolyte	YbScSZ	10 µm
2	AFL	NiO-YbScSZ	10 µm
3	Anode support	NiO-3YSZ+Carbon	120 µm

solvent, and dispersant were first ball-milled for 12 h using a zirconia ball and then, second ball-milling was conducted after adding a binder for 12 h. This method is designed to prevent the decline of degree of dispersion. After vacuum defoamation and filtering, the green sheet of 10 and 30 µm was fabricated by doctor blade method. The shear stress and viscosity at various shear rates were measured using a viscometer (DV-III, Brookfield, USA), and the coaxial cylinder type RV-29 was used as the spindle. To identify the sintering behavior the change of length was measured using a dilatometer (DIL 402C, Netzsch, Germany) using pellet type (Φ 5) raising the temperature until 1400 °C. The green sheet was pressed after laminating, and then cut. The fabricated green sheet was analyzed using a thermogravimetric analyzer to establish the degreasing condition of binder. The green sheet was laminated in the sequence as listed in Table 1 and then pressed. The green sheet was cut in 70×70 mm and sintered at 260 °C for 48 h to remove the binder. The microstructure of the green sheet and sintered body was measured using a scanning electron microscope (SEM) (JSM 6360, JEOL).

Results and Discussion

The basic experiments were performed with the emphasis on the thickness of green sheet and sinterability to select the conditions of mixing ratio of power/binder and solvent/binder are listed in Table 2 with 1.5 wt% dispersant addition according to the weight ratio of powder [11].

Fig. 1 shows the viscosities of the fabricated slurries were measured at various shear rates at 20 °C. The agglomeration is destroyed by the interaction between the particles in the slurry with increasing shear rate. Accordingly, the shear-thinning behavior was observed. By using the tape casting method, the slurry shows a low viscosity due to large shear stress during the forming.

Table 2. Slurry composition ratio and properties of Electrolyte,AFL and Anode support.

Function layer	Power/ Binder Ratio	Solvent/ Binder Ratio	Viscosity (cP,100 rpm)
Electrolyte	3.0	2.34	287
AFL	3.0	2.34	676
Anode support	3.2	2.25	798



Fig. 1. The slurry viscosity with rpm of electrolyte, AFL and anode support.



Fig. 2. SEM micrographs of electrolyte, AFL and anode support green tapes.



Fig. 3. Shrinkage profiles of electrolyte, AFL and anode support materials with the increase temperature.

However, the viscosity of slurry increased with decreasing shear stress of slurry after the forming. Therefore, we can confirm that the shear-thinning behavior for maintaining the shape of green sheet [12].

Fig. 2 shows the SEM images of the electrolyte,

anode-functional layer, and anode-support green sheets. The surface of the top and bottom shows similar microstructures without defect. Generally, when the dispersibility of slurry and dry conditions does not fit for the preparation of green sheet, the surface of the top and bottom microstructure was shown differently. In particular, when anode-support and activated carbon having different densities are mixed, the phase separation of slurry occurred. This phenomenon cause defects such as crack and agglomeration. The defects of green sheet can be solved by the optimization of binder content and dispersion of slurry.

Fig. 3 shows the electrolyte, anode-functional layer, and anode-support material heated up to 1400 °C, confirming the behavior of shrinkage according to temperature change. The 6Yb4ScSZ used as the electrolyte was rapidly contracted at 980 °C. The anode-functional layer of NiO-added 6Yb4ScSZ composition shows the rapid shrinkage at 850 °C. In particular, primary shrinkage of anode support containing activated carbon was about 11.3% from 100 to 400 °C. Although the secondary shrinkage started at 992 °C, the shrinkage shows the gentle behavior. In hetero-structure materials, the stress of sintered body was controlled by another combined material during the sintering process. It was also controlled by the relative thickness or volume. We can infer that the heating rate and sintering profile need to be controlled for the shrinkage in the temperature range of 850 to 1200 °C to suppress the phenomenon such as distortion or layer separation. Also, the optimization of sintering profile has to be considered for the shrinkage in the temperature range of 100 to 400 °C due to activated carbon of a relatively thick anode-support.

The electrolyte, anode-functional layer, anodesupport, and laminated unit cell were heated up to 1000 °C and then weight losses were confirmed with the temperature change, as shown in Fig. 4. It indicates that the weight losses of electrolyte and AFL were divided into two ranges of 280 to 360 °C and 360 to 600 °C. Therefore, the anode-support and laminated unit cell contain activated carbon. There are divided into two ranges of 280 to 360 °C and 360 to 800 °C, and 17.5% weight loss of binder containing activated carbon was observed. Most of the weight loss is known to occur by the solvent evaporation in the green sheet, thermal decomposition of organic matter, and carbon oxidation in the combustion process. In particular, laminated unit cell shows rapid weight loss in the range of 280 to 360 °C. Therefore, we can infer that time and temperature controls are necessary during the removal of binder. Moreover, the decomposition and carbonization of activated carbon is expected to occur in the temperature range of 600 to 800 °C. In this range, the porous structure as well as the removal of binder and control of profile to optimize the sintering shrinkage is important to anode-support.

Fig. 5 shows the sintering profile via the analysis of shrinkage and weight loss according to annealing



Fig. 4. Weight loss profiles of electrolyte, AFL and anode support materials with the increase temperature.

Fig. 5. Sintering profiles of co-firing electrolyte, AFL and anode support.

Fig. 6. The microstructure of co-fired unit cell at sintered temperature at $1350 \text{ }^{\circ}\text{C}$.

temperature. The removal of binder was maintained for 12 h after a heating rate of 1 °C/min. until 280 °C. The slow heating rate in the range of 280 to 1050 °C is advantageous to removal of organic binder and activated carbon used as porosity precursor. However, the temperature was increased as a heating rate of 5 °C/min. and maintained for 1h. in consideration of physical properties (flexure, layer separation, and crack), porosity, and density. At the temperature range of 1050 to 1350 °C, the temperature was increased as a heating rate of 2 °C/min. and maintained for 6 h to consider sintering shrinkage.

Fig. 7. The microstructures of electrolyte fracture depending on sintering temperatures (a) $1290 \,^{\circ}$ C (b) $1310 \,^{\circ}$ C (c) $1350 \,^{\circ}$ C (d) $1390 \,^{\circ}$ C.

Fig. 8. The microstructures of electrolyte fracture depending on sintering temperatures (a) 1290 $^{\circ}$ C (b) 1310 $^{\circ}$ C (c) 1350 $^{\circ}$ C (d) 1390 $^{\circ}$ C.

Fig. 6 shows the structure of unit cell composed of electrolyte, anode-functional layer, and anode-support without flexure, layer separation, and crack.

The microstructure was confirmed according to the temperature, as shown in Fig. 7. The dense structural property of electrolyte was important to preventing gas shift. The fine porosity was observed under 1310 °C. However, the fine porosity becomes smaller and dense structure was shown from 1350 °C.

Fig. 8 shows the microstructure of anode-functional layer with sintering temperature. It is important to obtain a dense microstructure to enhance the conductivity and the reliability of fuel cell [13]. The sintering temperature of NiO added anode-functional layer was lowered approximately 100 °C as shown in Figure. Therefore, the liquid phase and excessive-sintering microstructure is shown from 1350 °C.

Fig. 9 shows the anode support required a continuous porous structure can increase the transmissivity of gas and mechanical strength as well as the electrical conductivity at high temperatures. We can confirm that the stable pore distribution was shown until 1350 °C. In contrast,

Fig. 9. The microstructures of AFL fracture depending on sintering temperatures (a) 1290 °C (b) 1310 °C (c) 1350 °C (d) 1390 °C.

Fig. 10. Morphologies of unit cell (a) green unit cell (b) sintered unit cell.

the pores decreased because of grain growth at 1390 °C.

Fig. 10 shows the photograph of the unit cell before and after the sintering. The sintered body shows a final shrinkage of 21.8% without distortion and crack.

Conclusions

We can fabricate laminated unit cell composed of anode support, anode functional layer, electrolyte through various experiments. nThe mixing ratios of powder/binder, solvent/binder and viscosity conditions were optimized. From the shrinkage and weight loss profiles, the division of sintering temperature section and heating rate were controlled. As a result, compared with samples before sintering, the unit cell shows a final shrinkage of 21.8% after sintering.

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