Effect of pre-sintering of raw material powder on properties of solid oxide fuel cell electrolyte prepared by dip-coating method

Masaaki IZUMI[†] and Noboru SASAHARA*

Faculty of Environmental Engineering, The University of Kitakyushu,
1-1 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135

*Graduate School of Environmental Engineering, The University of Kitakyushu,
1-1 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135

In order to remedy defects of thin electrolyte films, which significantly affect the power generation performance of solid oxide fuel cells (SOFCs), the effects of pre-sintering of raw material powder (8 mol % Y_2O_3 -stabilized ZrO_2 : YSZ) on the properties of the electrolyte were investigated. After pre-sintering YSZ powder under various temperature and time conditions, electrolytes (about 30 μm in thickness) were deposited on the substrates of fuel electrodes by a dip-coating method and then co-sintered. The microstructures of the electrolytes were observed by scanning electron microscopy and laser scanning confocal microscopy. The power generation performance of fabricated cells was also investigated. As a result, the electrolyte fabricated by pre-sintering YSZ powder at 200°C for 120 h was found to be dense and impermeable. The cell containing the electrolyte showed reasonable power generation performance. In the case where the pre-sintering temperature was maintained at 200°C and the pre-sintering time was shortened to 20 h, the electrolyte was found to be porous, and the open circuit voltage of the cell was lower than the theoretical value. By increasing the pre-sintering temperature to 600°C for 20 h, an ideal electrolyte could be obtained. In contrast, the electrolyte fabricated using the YSZ powder without pre-sintering was highly porous, leading to a considerable drop in open circuit voltage.

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1. Introduction

Since solid oxide fuel cells (SOFCs) operate at high temperature, a high reaction rate and high energy conversion efficiency are ensured without the need for expensive catalysts such as platinum. The electrolyte management issues that arise with other types of fuel cells do not occur, because SOFCs are complete solid-state devices that use a ceramic material as the electrolyte. However, the high operating temperature poses problems of insufficient durability and reliability.^{1,2)}

To solve these problems, research and development of SOFCs has focused on the reduction of operating temperature. However, the reduction of operating temperature causes the increase of several overpotentials, especially of the ohmic loss of the electrolyte. The increase in the ohmic loss can be overcome by several measures such as the formation of thinner electrolytes³⁾⁻⁶⁾ and electrolytes with higher ionic conductivity.⁷⁾⁻¹⁰⁾ The use of thinner electrolytes can be realized by electrode-supported cells. However, using a thinner electrolyte in a cell increases the risk of deterioration in cell performance, because the presence of open pores in the thinner electrolyte increases the gas permeability of the electrolyte.

In this study, an electrolyte layer was deposited on a fuel electrode by a dip-coating method and then co-sintered. The effects of pre-sintering of the raw material powder of the electrolyte used for a suspension in the dip-coating method were investigated. The properties of the electrolyte were evaluated by scanning electron microscopy (SEM), laser scanning confocal

microscopy (LSCM), and the Vickers hardness test. The cell performance was also tested between 800 and 1000°C with humidified hydrogen as a fuel and air as an oxidant.

2. Experimental

2.1 Cell fabrication

Figure 1 shows the procedure for fabricating cells. The fuel electrode was extrusion-molded in the form of a flat plate after preparing a powder. The fuel electrode was made of NiO powder and YSZ (8 mol % Y_2O_3 -stabilized ZrO_2 , TZ-8YS, Tosoh Co.,

Fig. 1. Cell fabrication process.

[†] Corresponding author: M. Izumi; E-mail: izumi@env.kitakyu-u.ac.jp

Table 1. Conditions for pre-sintering YSZ (raw material) powder (○: investigated, ×: not investigated)

Temp.	Time		
	20 h	100 h	120 h
200°C	○	×	○
400°C	○	○	×
600°C	○	×	×

Ltd.) powder, which were mixed at a mass ratio of 1:1. The green substrates were produced by Kyushu Ceramics Industries Co., Ltd. Each of the green substrates, after drying, was heated at 1100°C in air. The heated substrate was dipped into an YSZ suspension and then dried. The YSZ suspension was prepared by mixing 8.4 g of YSZ powder with 200 cm³ of organic solvent (ethanol, >99.5%, Kanto Chemical Co., Inc.). An additional process was performed to dehydrate the organic solvent. The dipping and drying processes were repeated until the mass of deposited YSZ reached a prescribed amount. The green body of YSZ and NiO-YSZ laminate was co-sintered at 1450°C in air. Slurry which contained 100 g of La_{0.8}Sr_{0.2}MnO₃ powder (LSM-80, Daiichi Kigenso Kagaku Kogyo Co., Ltd.), 20 g of carbon as a pore-forming agent, and an adequate amount of alpha-terpineol was screen-printed as the air electrode onto the electrolyte and sintered at 1350°C in air. Finally, the electrolyte film on the opposite surface to the air electrode was removed by grinding.

The completed cell was 32 mm by 24 mm, and 1.2 mm in thickness. The electrolyte was about 30 μm in thickness. The air electrode was 10 mm by 10 mm, and 100–200 μm in thickness.

In this study, the YSZ powders of raw material used for the aforementioned dip-coating method were pre-sintered under various conditions as shown in **Table 1**. The effects of the pre-sintering on properties of the electrolyte were examined and also compared with the case in which the YSZ powder was not pre-sintered.

2.2 Evaluation of electrolyte

The microstructure of the electrolyte surface was observed by SEM. The surface roughness of the electrolyte was also measured by LSCM. The surface roughness was measured for five lines of 128 μm in length on each specimen, and then averaged. The Vickers hardness of the electrolyte was measured at five points on each specimen under the condition of a load of 9.8 N, and then averaged. The specimens without the air electrodes after the formation of the electrolyte were used for the SEM observation, the roughness and hardness tests.

The cell performance (*I*–*V* characteristics) was measured at 800–1000°C while controlling the generated current with an electric-load device. The fuel cell was fed with H₂ as a fuel gas at a flow rate of 100 ml/min after humidifying H₂ at room temperature. Air fed to the fuel cell at a flow rate of 100 ml/min was used as the oxidant. The measured open circuit voltage (OCV) was compared with the theoretical value *E*, which was calculated using the following equation.¹¹⁾

$$E = \frac{RT}{4F} \ln \left(\frac{p_{O_{2,c}}}{p_{O_{2,a}}} \right) \quad (1)$$

Here, *R* is the gas constant, *T* is the operating temperature, *F* is the Faraday constant, and *p*_{O₂} is the partial pressure of oxygen. The subscripts of *a* and *c* denote the sides of the fuel electrode and the air electrode, respectively.

Fig. 2. SEM images of electrolyte surface: (a) without pre-sintering, (b) pre-sintered at 200°C for 20 h, and (c) pre-sintered at 200°C for 120 h.

3. Results and discussion

Figure 2 shows SEM images of the electrolyte surfaces. **Figure 2(a)** shows a SEM image of the electrolyte formed using the YSZ powder that was not pre-sintered. The microstructure of the electrolyte is highly porous and has some large pores. Although the electrolyte is improved by pre-sintering at 200°C for 20 h, some small pores are still observed as shown in **Fig. 2(b)**. However, **Fig. 2(c)** shows that the YSZ powder can be sintered to form a YSZ electrolyte film that is extremely dense by extending the pre-sintering time and maintaining a pre-sintering temperature of 200°C.

Figure 3 shows the results of the surface roughness of the electrolyte film measured with the LSCM. The average maximum height *R_z* of the electrolyte film obtained using the YSZ powder pre-sintered at 200°C for 20 h is 1.2 μm. The values of *R_z* are almost independent of temperature and time for pre-sintering

Fig. 3. Maximum height of surface roughness R_z . Fig. 4. Vickers hardness H_v of electrolyte (9.8 N load).

performed in the range of this study. However, when the YSZ powder was used without pre-sintering, the value of R_z increased significantly.

As shown in **Fig. 4**, the Vickers hardness H_v of the electrolyte formed by pre-sintering at 200°C for 20 h is 1241. By extending the pre-sintering time to 120 h at the same temperature of 200°C, H_v increases to 1444, which is about 1.2 times that of the above value. In the case of 20 h, H_v increases from 1241 to 1354 when the pre-sintering temperature is increased from 200 to 400°C. The depth of the indentation made with the indenter was estimated to be less than 6 μm judging from the length of the diagonal line of the indentation. The depth was less than the electrolyte thickness of approximately 30 μm. Thus, although the specimen was a laminate composed of the electrolyte and the fuel electrode, the hardness of only the electrolyte could be measured.

An example of the I - V (current density-terminal voltage) characteristics is shown in **Fig. 5**. This performance was measured with the cell fabricated using the YSZ powder pre-sintered at 200°C for 120 h. The I - V characteristics of the cells fabricated by pre-sintering at 400°C for 100 h and 600°C for 20 h were similar to those shown in Fig. 5. However, the performances of the cells fabricated by pre-sintering at 200°C for 20 h, at 400°C for 20 h, and without pre-sintering were considerably lower than those under the aforementioned three conditions.

Figure 6 shows the relationship between the theoretical OCV (open circuit voltage) and the measured OCV. The measured OCVs under both the conditions without pre-sintering and at 200°C for 20 h are much lower than the theoretical values. However, when the pre-sintering time is extended to 120 h, the measured OCVs at 200°C are close to the theoretical values. The good agreement between the measured OCVs and the theoretical

Fig. 5. I - V characteristics of cell (pre-sintered at 200°C for 120 h).

Fig. 6. Comparison of measured OCV with theoretical OCV (operating temperature: 800–1000°C).

Fig. 7. TG curve of YSZ raw material powder (rate of temperature rise: 10.0°C/min, initial mass of sample: 22.062 g).

OCVs indicates that the electrolytes are dense and have no cross-leakage of gases. The results correspond to the SEM images as shown in Fig. 2. In the case of a pre-sintering time of 20 h, the measured OCV is close to the theoretical value by increasing temperature to 600°C.

Pre-sintering causes the decrease of mass of the raw powder of YSZ as shown in **Fig. 7** (thermo-gravimetric curve). The mass of YSZ powder decreases with increasing temperature up to about 200°C, and then reaches a minimum. Judging from this result and the evaluation of the electrolytes, it seems likely that the raw powder has some absorbed water and its water has an effect on the sintering of the YSZ powder. However, there was no remarkable difference between the SEM image of the pre-sintered YSZ powder and that of the YSZ powder that was not pre-sintered. When comparing the SEM images of the depositional surfaces after dip-coating and before co-sintering, also, the surface appearance of the deposit made of the pre-sintered YSZ powder was not significantly different from that made of the YSZ powder that was not pre-sintered. More detailed investigations are necessary to reveal the relationship between the sintering of the YSZ powder and the absorbed water.

4. Conclusions

When the YSZ electrolyte was deposited by a dip-coating method, the properties of the electrolyte depended on the process of pre-sintering of the YSZ raw material powder used in the suspension for the dip-coating method. The electrolyte fabricated using YSZ powder after pre-sintering at 200°C for 120 h was dense and impermeable. The cell containing the electrolyte showed reasonable power generation performance. When the time for pre-sintering was shortened to 20 h and the pre-sintering temperature was 200°C, the electrolyte was found to be porous and the open circuit voltage of the cell was lower than the theoretical value. By increasing the pre-sintering temperature to 600°C for a pre-sintering time of 20 h, an ideal electrolyte could be obtained. In contrast, the electrolyte fabricated using the YSZ powder without pre-sintering was

very porous, and caused a considerable drop in open circuit voltage.

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