

Effect of cosintering of anode–electrolyte bilayer on the fabrication of anode-supported solid oxide fuel cells

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Abstract A comparative study is carried out on the effect of cosintering temperature of anode–electrolyte bilayer on the fabrication and cell performance of anode-supported solid oxide fuel cells from commercially available tape casting materials. It was found that the sintering conditions have profound effects on the anode characteristic and cell performance. For low cosintering temperature as low as 1,250 °C, the electrolyte is unable to sinter fully and forms a porous structure which leads to a reduced open-circuit potential and poor cell performance especially under low current output. For further increasing cosintering temperature to 1,350 °C, the cell performance was lower under low current operation. However, the cell performance turns out to be better than that of high-temperature cosintering under high current output. Although at temperature as high as 1,500 °C the cell performs better than that of low temperature cosintering, the trend turn out to be reverse for high current operating due to less anode surface area resulting from overagglomeration of anode layer. An optimal cosintering temperature of 1,350–1,450 °C is recommended for commercially available anode–electrolyte bilayer of anode-supported solid oxide fuel cells.

Keywords Anode-supported solid oxide fuel cells · Cosintering · Anode–electrolyte bilayer · Proton exchange membrane fuel cell (PEMFC) · Direct methanol fuel cell (DMFC)

Introduction

Because of their potential to reduce the environmental impact and geopolitical consequences of the use of fossil fuels, fuel cells have emerged as attractive alternatives to combustion engines. Like a combustion engine, a fuel cell uses some sort of chemical fuel as its energy source. More like a battery, the chemical energy is directly converted to electrical energy, without an often messy and relatively inefficient combustion step. In addition to high efficiency and low emissions, fuel cells are attractive for their modular and distributed nature and zero noise pollution. They will also play an essential role in any future hydrogen fuel economy. Among all the popular fuel cells developed internationally, solid oxide fuel cells (SOFCs) provide high energy conversion efficiency due to direct conversion of fuels into electric power at high temperature in a cogeneration system comparing to that of low temperature proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs).

Conventional SOFCs with an yttria-stabilized zirconia (YSZ) electrolyte are now being operated at 900 °C or higher temperature to attain power density sufficient to use in the system. However, the high-temperature operation causes serious problems such as internal mechanical stress due to the difference in the thermal expansion coefficients of the materials and chemical reactions. Therefore, operating temperature lower than 700 °C is desirable [1]. Because electrochemical and conduction processes in SOFC are strongly thermally activated, a reduced operating temperature leads to another difficulty in large voltage losses due to the ohmic resistance of the materials and the polarization at the electrodes. Most of the voltage losses are generated from the ohmic resistance of the electrolyte, a number of approaches have been reported preparing a thinner electro-

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lyte which reduces the corresponding resistance [2, 3], and high power density was obtained using YSZ thin-film electrolytes [4, 5]. There are generally two categories making a robust anode–electrolyte–cathode cell while maintaining thin electrolyte layer: cathode-supported cell [6, 7] and anode-supported cell [8–10]. Despite the fact that cathode-supported cell can be produced by ceramic process (Toho) as well as by atmospheric plasma spraying (Siemens-Westinghouse) with scalable processes, most studies focus on anode-supported cell structure because thicker anode can be designed with good thermal coefficient of expansion match to the electrolyte, and it has excellent conductivity. In addition, an anode-supporting structure presents advantages in terms of cost, conductivity, and mechanical strength. Moreover, the anode support allows film deposition of the electrolyte by easily scalable and automated (high temperature) ceramic processes, as opposed to expensive and production-limiting vapor deposition techniques (physical vapor deposition, electrochemical vapor deposition) of thin YSZ employed at necessarily lower temperature for cathode supports. Although anode-supported cell possesses advantages compared to that of cathode- and electrolyte-supported cell, some disadvantages including high NiO content, lack of redox stability, and low mechanical stability needed to be overcome for ultimate commercialization.

Various processes have been investigated as the manufacturing process of anode-supported SOFCs. Among them, a wet process is especially attractive because of its low cost and mass productivity. Cosintering of electrolyte and anode substrate is widely adopted for this purpose, and robust structures and high performances are reported [11–14]. The sintering temperature for such structure is generally in the range of 1,350–1,450 °C in order to form a dense electrolyte and a good electrode and electrolyte interfacial contact. However, optimal information regarding every single component including the material processing–fabrication parameters–cosintering temperatures, microstructure, and composition of electrodes are limited to the material compositions made by individual groups. And this presents difficulties for other groups to reproduce the same results. Considering the successful research progress undergoing in PEMFC and DMFC using commercially available materials (e.g., Dupont Nafion as electrolyte and E-TEK Pt/C as electrode catalyst) as a basis and fabricate electrolyte-supported cell for performance evaluation [15–17], the aim of this study was to obtain more information about the contribution of cosintering temperature to the electrochemical performance of anode-supported SOFC currently manufactured as standard materials of ESL Co., Ltd. Cosintering temperatures between 1,200 °C and 1,600 °C are used for evaluating effects of cosintering temperatures on the anode-supported SOFC.

Experimental

Cell fabrication

Green films of the electrolyte tape (42400, 8 mol% YSZ, thickness=0.07 mm, ESL Electro-Science Co. Ltd), anode tape(42420, NiO/YSZ=30/70 wt.%, thickness=0.07 mm, ESL Electro-Science Co. Ltd), and porous anode tape (42421, NiO/YSZ=30/70 wt.%, thickness=0.18 mm, ESL Electro-Science Co. Ltd) were cut to the dimensions of 40×40 mm. The three tapes were then laminated via hot-pressing at 1,000 psi, 70 °C and stayed for 20 min. The firing profiles are as follows: (a) first, firing step from 25 °C to 650 °C with the heating rate controlled at 0.9~1.1 °C/min; (b) second, firing step from 650 °C to target temperatures (1,200–1,600 °C) with the heating rate controlled at 3~5 °C/min; (c) third, the cell was maintained at target temperatures for another 120 min; (d) the final step is cooling. After that, (La, Sr)MnO₃ (LSM) paste (42400, ESL Electro-Science Co. Ltd), which was selected as cathode material, was printed onto the YSZ electrolyte pellets, and they were fired at 1,200 °C and stayed for 120 min. Figure 1 shows the photograph of the anode-supported SOFC in this study.

Density and surface area measurement

Green electrolyte–anode–porous anode multilayers of these separated samples were calcined at 1,250, 1,300, 1,350 °C, 1,400 °C, 1,450 °C, 1,500 °C, 1,550 °C, and 1,600 °C in air for 120 min with a heating rate of 5 °C/min. LSM cathode paste was printed on the electrolyte surface of postsintered electrolyte–anode–porous anode multilayers and were fired at 1,200 °C. The resultant sintered densities (D_{rs}) of the

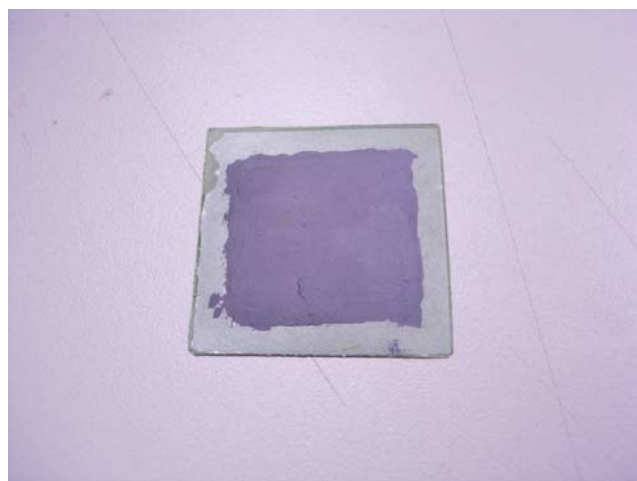


Fig. 1 Photograph of anode-supported cell (as prepared)

cells for both postsintered and postpretreatment were measured by the Archimedes method,

$$D_{rs} = \frac{W_1 \rho}{W_2 - W_3} \quad (1)$$

where W_1 is the dry weight, W_2 is the wet weight (water in body), W_3 is the body's submerged weight without fine wire, and ρ is the density of the solvent (water). Considering the high volume and weight percentage of anode among anode-supported cell, the density change is primarily due to variation of anode structure. In addition, the surface area of anode was confirmed by Brunauer–Emmett–Teller absorption isotherm method using N_2 gas before the application of cathode layers.

Microstructural characterization

The morphology of the anode surfaces were studied by means of a scanning electron microscope (SEM, model JSM-5600, Jeol Co., Japan) equipped with energy-dispersive spectroscopy. The anode surface was coated with gold powder under vacuum.

Conductivity measurements

Electrical conductivity of anode was measured by the four-terminal method. The sintered samples were around the size of approximately $4 \times 4 \times 0.1$ -mm dimensions. The potential and current leads were contacted by applying platinum paste and fixing to metallic platinum.

Anode pretreatment and cell testing

Electrochemical measurements of the anode-supported cells were performed in a stainless steel test fixture placed inside the high-temperature furnace. In order to obtain sufficient electronic contact between the cell and the electronic devices, Au meshes were used on both side of the anode and the cathode. Two platinum wires were connected to each Au mesh to serve as respective voltage and current probes. Sealing of the gas compartment was performed by YSZ fibers doped with YSZ powder (Z-Car Co., USA). At the beginning of the tests, an argon flow was introduced at the anode side and an air flow at the cathode side. The temperature was then slowly increased to 500 °C for anode pretreatment. After reaching this temperature, the anode of the single cells was reduced by a stepwise replacement of argon by 10 vol.% hydrogen. The total gas flows of hydrogen and air were both set at 150 ml/min (standard temperature and pressure) using mass flow controllers. The NiO in the anode was reduced to Ni, in situ. All electrochemical data obtained after the pretreatments were by direct current methods using a current-control power supply and a computer-controlled data

acquisition system. The current–voltage characteristics were measured with increasing current load by a sequential step change of 0.05 V starting from 1.0 V until the voltage dropped below 0.2 V.

Result

Current–voltage characteristics

The performance results of anode-supported cells with various anode–electrolyte cosintering temperatures started from 1,250 °C to 1,550 °C are shown in Fig. 2. It is found that open-circuit voltage (OCV) of anode-supported cells with low anode sintering temperature (e.g., 1,250 °C) is lower. The OCV for cosintering temperature at 1,250 °C is about 0.784 V and is notably lower than that of others. In addition, the average current output is 0.03 A/cm² for the voltage of 0.2 V and presents an unusual trend of increasing current output compared to that of others. The extraordinary lower OCV and performance result from less-compact electrolyte layer as a consequence of insufficient cosintering temperature. The less-compact electrolyte layer will lead to crossover of fuel and oxidant and mix potential hereafter. The OCV is further increased to 0.83 V with one additional electrolyte as shown in Fig. 3. However, cell with two electrolytes results in lower performance compared to that of cell including one electrolyte due to higher ohmic resistance.

By increasing the cosintering temperature to 1,300 and 1,350 °C, the cell performance increases further as well as the OCV. The current density at 0.3 V is 0.04 A/cm² and 0.05 A/cm² for cosintering temperature at 1,300 and 1,350 °C, respectively. This is one solid proof that higher cosintering temperature enhanced cell structure and especially electrolyte. The performances for the cosintering temperature of 1,400 °C and 1,450 °C present a similar

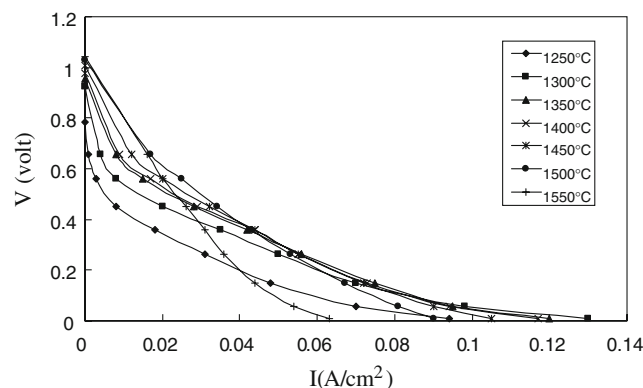


Fig. 2 I–V characteristics of anode-supported cell based on various anode–electrolyte cosintering temperature

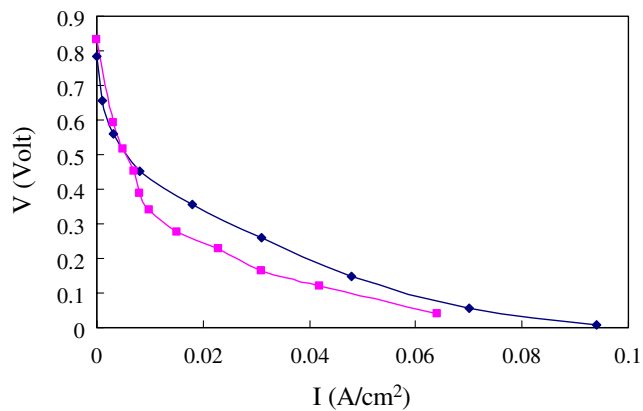
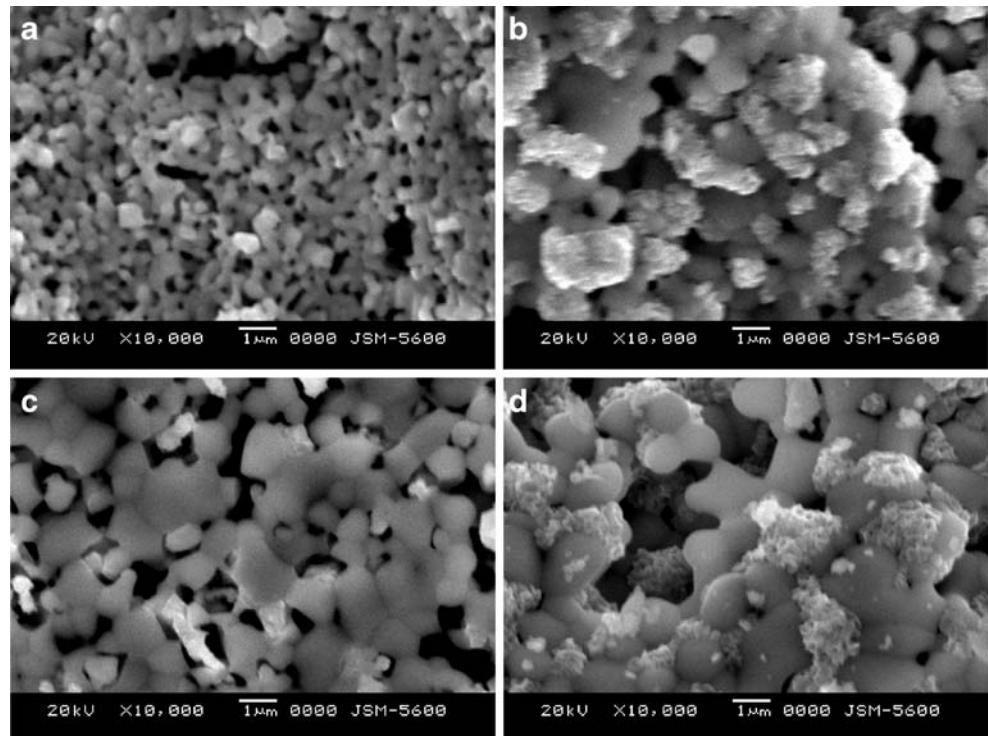


Fig. 3 The OCV and I–V characteristics of anode-supported cell with various electrolyte layers: (filled square) two electrolyte, (filled diamond) one electrolyte

trend to that of 1,350 °C; however, performance for the cosintering temperature of 1,500 °C present a slightly different trend to that of 1,350 to 1,450 °C. It was found that, as the cosintering temperature increased, the SOFC performance improves slightly at the low current density region and reduces gradually at the high current density region. The open-circuit voltage also increases from 0.9 to 1.0 V with increasing cosintering temperature from 1,400 °C to 1,500 °C, revealing that anode-supported cell at higher cosintering temperature has a higher potential to resist the fuel crossover from anode to cathode and this will result in higher cell performance at lower current density. However, at higher current density, the surface area for the anode reaction is also decreased for high cosintering temperature. This results in

Fig. 4 Series of SEM photographs for samples with various sintering temperatures: **a** 1,250 °C, **b** 1,350 °C, **c** 1,400 °C, and **d** 1,450 °C



insufficient surface area and lowering the cell performance. By increasing the cofiring temperature to 1,550 °C, the cell performance decreases particularly under high current density operation.

Effect of cosintering temperature on microstructural properties

Figure 4 shows series of SEM photographs which were all taken with the same magnification ($\times 10,000$) and depict typical areas of the microstructure of each of the sample used in the performance measurements. As shown in Fig. 4, the grain size for anode side sintering at temperature of 1,250 °C is quite small. As the cosintering temperature is raised to 1,350 °C and 1,400 °C, there is a significant grain growth. The grain size does not reveal further growth as the cosintering temperature further increased to 1,450 °C; however, some small particles reveal serious agglomeration locally. The agglomerated particles are attributed to Ni which are thermally activated to move freely especially under cosintering temperature higher than 1,450 °C. The resulting agglomerated Ni will results in insufficient surface area to accomplish electrochemical reaction for high current output as has been addressed in “Current–voltage characteristics”.

Density of anode-supported cells

Figure 5 presents the measured densities of the anode-supported cells fired from 1,300 °C to 1,600 °C in air for

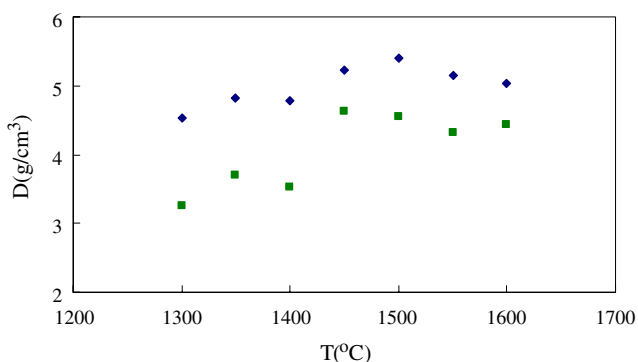


Fig. 5 Density distributions of anode of postsintering (*filled diamond*) and postpretreatment (*filled square*) for cosintering at different temperature

both postsintered and postpretreatment. For the cosintering temperature of 1,300 °C, the density is about 4.5 g/cm³. The density increases further with increasing temperature to 1,500 °C for a value of 5.5 g/cm³, about 22% increase. Apparently, there is a big jump for sintering temperature from 1,400 to 1,500 °C. The density increase with increasing cosintering temperature was due to agglomeration of anode materials and became more pronounced for temperature higher than 1,400 °C. For cosintering temperature higher than 1,500 °C, the anode density drops slightly to 5.2 and 5.0 g/cm³ for the cosintering temperature of 1,550 °C and 1,600 °C, respectively. The anode-supported cell densities after pretreatment at 500 °C with continuous dilute H₂ flowing for 12 h are also shown in Fig. 5. The trend is similar to that of postsintered anode-supported cells. For the cosintered temperature of 1,300 °C, the density is lowered to 3.2 from 4.5 g/cm³ due to NiO reducing to Ni. The density difference between postsintered and postpretreatment anode is about 1.3 g/cm³. By increasing cosintering temperature, the density difference between postsintered and postpretreatment anode becomes smaller. The result is easy to explain that as anode materials agglomerated with increasing temperature, the resulting compact anode structure leads to difficult NiO reduction process. Therefore, incomplete anode reduction concluded and less-porous anode structure resulted.

Surface area

Figure 6 shows the surface area of the anode after cosintering at different temperatures. The highest surface area of 5.9 m²/g was reached for the cosintering temperature of 1,300 °C and decreased gradually to 3.3 and 2.5 m²/g for the cosintering temperature of 1,400 °C and 1,500 °C, respectively. For further increasing the cosintering temperature to 1,600 °C, the surface area decreases sharply to 1.6 g/cm³. The surface area decreases with increasing cosintering temperature was due to agglomeration of anode

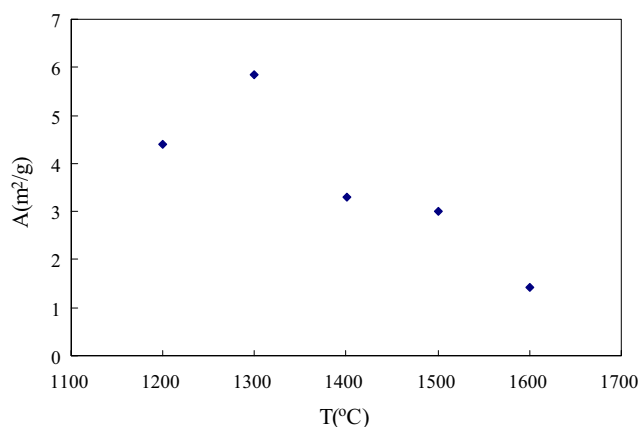


Fig. 6 Surface area distribution of anode for cosintering at different temperature

materials and primarily attributed to Ni. It is found that the overagglomeration of Ni is especially serious for cosintering temperature higher than 1,500 °C, and this will result in insufficient surface area to accomplish electrochemical reaction for high current output as has been addressed in “Current–voltage characteristics” and “Effect of cosintering temperature on microstructural properties.”

Conductivity

In this section, electrical conductivity of anode sintered at different temperature was measured. The microstructure of anode changed during sintering process has been found from previous section, and the change will influence the anode conductivity and cell performance hereafter.

As shown in Fig. 7, conductivity for cosintering temperature of 1,200 °C is 137.3 S/cm and increased to 219.8 S/cm at 1,300 °C. As the cosintering temperature increases further to 1,400 °C and 1,500 °C, the conductivity increases further to 350 S/cm and 470 S/cm, respectively. The conductivity increasing rates are 83, 130, and 120 S/cm °C

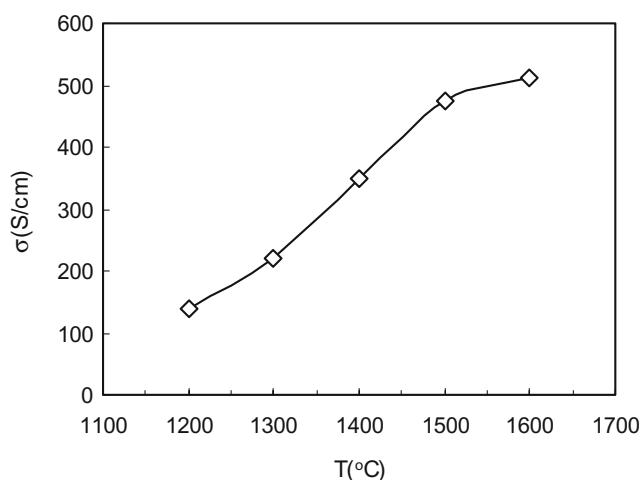


Fig. 7 Conductivity distribution of anode for cosintering at different temperature

for the cosintering temperature ranges of 1,200–1,300 °C, 1,300–1,400 °C, and 1,400–1,500 °C, respectively. Obviously, as the cosintering temperature becomes higher than 1,300 °C, the anode structure agglomerated greatly and resulted in continuous conducting network compared to that of sintered temperature lower than 1,300 °C. The effect of cosintering temperature on anode structure and its conductivity can be correlated by comparing SEM and conductivity results. The anode structure for low temperature (e.g., 1,250 °C) is loosened and agglomerated largely as cosintering temperature becomes higher than 1,350 °C as shown in Fig. 4. In addition to the anode agglomeration primarily from YSZ, Ni diffuses and sinters easily and results in good Ni networking for better electrical conductivity [18].

Conclusion

At this point of the study, performances are not optimized and low power densities are available due to dilute H₂ used and lower operation temperature in this study. However, cosintering temperatures are proven to have pronounced effect on the fabrication and characterization of an anode-supported cell. For cosintering temperature as low as 1,250 °C, the electrolyte is unable to sinter fully and forms a porous structure which leads to a reduced open-circuit potential and poor cell performance especially under low current output. For cosintering temperature higher than 1,500 °C, the cell performance decreases particularly under high current density operation due to overagglomeration of anode structure. Accompanying with SEM, surface area, and conductivity results, an optimal cosintering temperature of 1,350–1,450 °C is recommended for commercially available anode–electrolyte multilayer for anode-supported SOFC to achieve acceptable performance. This is essentially impor-

tant for SOFC community to use commercially available materials instead of using materials developed by individual groups and to speed up research and development of anode-supported SOFC technology.

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