Anode-supported Type SOFCs based on Novel Low Temperature Ceramic Coating Process

Jong-Jin Choi†, Cheol-Woo Ahn, Jong-Woo Kim, Jungho Ryu, Byung-Dong Hahn, Woon-Ha Yoon, and Dong-Soo Park

Functional Ceramics Department, Korea Institute of Materials Science, Changwon 51508, Korea

(Received July 28, 2015; Revised August 27, 2015; Accepted August 29, 2015)

ABSTRACT

To prevent an interfacial reaction between the anode and the electrolyte layer during the conventional high-temperature co-firing process, an anode-supported type cell with a thin-film electrolyte was fabricated by low-temperature ceramic thick film coating process. Ni-GDC cermet composite was used as the anode material and YSZ was used as the electrolyte material. Open circuit voltage and maximum power density were found to strongly depend on the surface uniformity of the anode functional layer. By optimizing the microstructure of the anode functional layer, the open circuit voltage and maximum powder density of the cell increased to 1.11 V and 1.35 W/cm², respectively, at 750°C. When a GDC barrier layer was applied between the YSZ electrolyte and the LSCF cathode, the cell showed good stability, with almost no degradation up to 100 h. Anode-supported type SOFCs with high performance and good stability were fabricated using a coating process.

Key words: SOFC, Anode-supported type, Coating, Low temperature process

1. Introduction

Solid oxide fuel cells (SOFCs) are promising new electric power generation systems mainly because they have high energy conversion efficiency and fuel flexibility. Over the last several decades, global development and industrializing activities in the field of SOFCs have been dominated by electrolyte supported cells (ESC) and anode-supported cells (ASC). In the case of ESCs, the mechanical support part is a dense electrolyte with a thickness of at least 200 µm or higher. Because the whole cell's resistance and the overall cell performance strongly depend on the electrolyte thickness, an ASC structure is suggested and developed in an attempt to reduce the electrolyte thickness. To sufficiently densify the electrolyte so as to prevent mixing of air and fuel, the ASC structure generally requires co-firing of the electrolyte and anode at the highest processing temperature in the entire cell process. In the case of ESCs, the electrolyte and electrode sintering steps can be separated, so it is possible to decrease the interface reaction because porous electrodes require lower firing temperatures than that required by the electrolyte (Fig. 1). The co-firing temperature in ASC processing depends on the electrolyte materials, but is generally higher than 1400°C. This high co-firing temperature limits material choice due to interfacial reactions that generally form low-conductivity second phases. For example, even though usage of GDC as an anode material confers several advantages such as good ionic conductivity and stability against carbon coaking, this process is not recommended for the sintering of a YSZ and a GDC together at a temperature higher than 1200°C due to La₂Zr₂O₇, SrZrO₃ formation. Also, it is well known that the LSGM perovskite electrolyte has high reactivity with the Ni-containing anode. To avoid these reactions, an economical lower-temperature ceramic consolidation process is required. Metal supported-type cells (MSC), which are made with cheaper and robust porous metal support and thin film ceramic components, face processing challenges due to limitations of the sintering conditions in reducing atmosphere; these cells also have the problem of metal/anode interface reaction. SOFCs that include thin electrolytes are commonly manufactured using wet ceramic processing techniques such as tape casting and screen printing, with the layers co-fired at temperatures up to 1400°C. However, such multilayer sintering processes are laborious, costly, and difficult to automate. High-temperature sintering can cause problems such as undesirable interfacial reactions, warping of large-plate anodes, and grain growth of Ni phases in the anode substrate. Various deposition techniques have been developed as alternatives to co-firing for the fabrication of thin film electrolytes; these techniques include electrochemical vapor deposition, physical vapor deposition, electrophotoretic deposition, spray pyrolysis, modified sol-gel deposition, and vacuum plasma spraying. Due to the high costs and limited deposition areas of these processes, they tend to produce films that are not sufficiently dense and not scalable for mass-production.

†Corresponding author: Jong-Jin Choi
E-mail: finaljin@kims.re.kr
Tel: +82-55-280-3371 Fax: +82-55-280-3392
For these reasons, for SOFC applications, we have tried to apply a novel economical ceramic coating technique operating at room temperature using a granule spray in vacuum (GSV). The GSV process is a kind of room-temperature ceramic spray coating process in low vacuum conditions, typically at 1~10 torr. The granule, which is intentionally agglomerated fine ceramic particles, is mixed with the carrier gas and forms an aerosol flow. The formed aerosol flow is accelerated by the pressure difference between the aerosol chamber and the deposition chamber; the aerosol is then ejected through the nozzle with high kinetic energy. The aerosol collides with the substrate and forms a dense ceramic film without external heating. This process uses a relatively cheap, micron-sized engineering ceramic powder. This process can be used to cover large areas with high deposition rate; therefore, it is appropriate for commercialization. The deposition mechanism is closely related to the fracturing and plastic deformation of the primary particles. High deposition rates (> 10 mm/min) can be achieved with no additional heating required for the solidification of the ceramic powder; this solidification process might otherwise bend or distort the layered structures of solid oxide fuel cells.

This study reports the fabrication of ASC based on the GSV process operating at room temperature. As anode support, an NiO-GDC composite with gradient porosity was prepared using the conventional tape-casting process. An anode support including an anode functional layer (AFL) and a support layer was fabricated by tape-casting, laminating, and co-firing. For anode support fabrication, 27 wt% of NiO (A grade, Novamet), 18 wt% of GDC (ULSA, Rhodia), 5 wt% of polymethyl methacrylate (S50, Sunjin Chem.) as a pore former, and 50 wt% of a commercial binder system (B73225, Ferro) were mixed for 4 h by planetary milling using zirconia balls as milling media. For the AFL fabrication, various compositions and particle sizes of NiO and GDC powders were tested, including NiO of Kojundo, Kceracell AFL grade, and GDC of Rhodia ULSA, FCM-m. The NiO and GDC powders were mixed for 4 h with various amounts of commercial binder system using the planetary milling machine with zirconia balls as milling media.

The thicknesses of the prepared tapes of the NiO-GDC support and the AFL layers were 85 and 25 µm, respectively. Twelve layers of support and 2 layers of AFL tape were laminated and warm-pressed at 50°C in a 30-mm-diameter mold for 10 min at a pressure of 5 tons. Binder burn-out of the laminated structure was conducted in ambient atmosphere at 260, 700, and 1000°C, respectively, for 2 h; material was finally sintered at 1350°C for 2 h. All heating processes were conducted in one step, sequentially.

Electrolytes were deposited using commercially available YSZ (FYT13.0-005H, Unitec Ceramics) as a starting powder. Granules with average sizes of ~100 µm were prepared using a conventional disk-type nozzle system. The dried YSZ granule was mixed with carrier gas to form an aerosol flow in the aerosol chamber. The aerosol flow was transported through a tube to the nozzle before being accelerated and ejected into the deposition chamber through a rectangular nozzle with a 25 × 0.8 mm² orifice, which was evacuated by a rotary pump with a mechanical booster. Compressed air was dried through a dehumidifying filter and used as the carrier gas at a flow rate of 15 l/min. The pressures in the aerosol and deposition chambers were 600 and 1 torr, respectively. The accelerated YSZ granules collided with the prepared anode support structure, which was located 5 mm from the nozzle. Cathode layers were then prepared on the YSZ film using commercially available LSCF powder (LSCF-S, Keracell), which was heat-treated and mixed.

2. Experimental Procedure

An anode support including an anode functional layer (AFL) and a support layer was fabricated by tape-casting, laminating, and co-firing. For anode support fabrication, 27 wt% of NiO (A grade, Novamet), 18 wt% of GDC (ULSA, Rhodia), 5 wt% of polymethyl methacrylate (S50, Sunjin Chem.) as a pore former, and 50 wt% of a commercial binder system (B73225, Ferro) were mixed for 4 h by planetary milling using zirconia balls as milling media. For the AFL fabrication, various compositions and particle sizes of NiO and GDC powders were tested, including NiO of Kojundo, Kceracell AFL grade, and GDC of Rhodia ULSA, FCM-m. The NiO and GDC powders were mixed for 4 h with various amounts of commercial binder system using the planetary milling machine with zirconia balls as milling media.

The thicknesses of the prepared tapes of the NiO-GDC support and the AFL layers were 85 and 25 µm, respectively. Twelve layers of support and 2 layers of AFL tape were laminated and warm-pressed at 50°C in a 30-mm-diameter mold for 10 min at a pressure of 5 tons. Binder burn-out of the laminated structure was conducted in ambient atmosphere at 260, 700, and 1000°C, respectively, for 2 h; material was finally sintered at 1350°C for 2 h. All heating processes were conducted in one step, sequentially.

Electrolytes were deposited using commercially available YSZ (FYT13.0-005H, Unitec Ceramics) as a starting powder. Granules with average sizes of ~100 µm were prepared using a conventional disk-type nozzle system. The dried YSZ granule was mixed with carrier gas to form an aerosol flow in the aerosol chamber. The aerosol flow was transported through a tube to the nozzle before being accelerated and ejected into the deposition chamber through a rectangular nozzle with a 25 × 0.8 mm² orifice, which was evacuated by a rotary pump with a mechanical booster. Compressed air was dried through a dehumidifying filter and used as the carrier gas at a flow rate of 15 l/min. The pressures in the aerosol and deposition chambers were 600 and 1 torr, respectively. The accelerated YSZ granules collided with the prepared anode support structure, which was located 5 mm from the nozzle. Cathode layers were then prepared on the YSZ film using commercially available LSCF powder (LSCF-S, Keracell), which was heat-treated and mixed.

Fig. 1. Schematics of electrolyte-supported and anode-supported cells.
with polyvinylidene fluoride (PVDF, Aldrich) at a weight ratio of 19:1. The PVDF polymer decomposed during evaluation of the resulting SOFCs to form nano-sized porous structures. The schematics of the coating equipment are shown in Figs. 2, 3 summarizes the sample images of each preparation step for the full cell fabrication process. The cell diameter, thickness, and cathode area were 25 mm, 1.0 mm, and 1.0 cm², respectively.

Surface and fractured cross section microstructures of the films were examined using a scanning electron microscope (SEM, JSM-5800, JEOL) and a scanning transmission electron microscope (STEM, JEM-2100F, JEOL) equipped with an energy dispersion X-ray (EDX) spectrometer. For electrochemical testing of the cell, Pt mesh with small amounts of Pt paste attached as current collectors were employed at both the cathode and anode sides. A Pyrex ring was used for gas sealing between the electrolyte and the alumina tube of the sample holder. Air oxidant and dry H₂ fuel were used at flow rates of 1000 and 200 ccm, respectively. The cells’ current-voltage (I-V) characteristics at 750°C were recorded at a scan rate of 10 mA/s; impedance spectra were measured using an electrochemical impedance spectroscope analyzer (SP300, Biologic) over a frequency range of 30 mHz - 1 MHz, with a potentiostatic mode of 0.7 V.

3. Results and Discussion

Figure 4 provides a sample image and analysis results for the YSZ electrolyte film deposited on sapphire substrate for microstructural observation, phase analysis, and ionic conductivity measurement. Fig. 4(a) shows the translucent YSZ film deposited on the sapphire substrate. Fig. 4(b) shows the microstructure of the powder used for deposition; this powder had an average particle size of ~1.53 µm. Figs. 4(c) and 4(d) provide SEM and TEM cross-sectional observations of the film, respectively. Both figures show a fairly dense microstructure with grain size of less than 20 nm, far smaller than that of the initial powder, which formed by collisions of the particles induced by the kinetic energy of the initial particles. Fig. 4(e) shows XRD analysis images of the powder, the as-deposited film, and the post-annealed film. The deposited films showed similar cubic fluorite structures with smaller and broader peaks in their spectra due to the smaller crystallites that formed during deposition. The peaks of the film were shifted to lower angles due to residual compressive stress induced during deposition. Post-annealing of the film made the peaks sharper and caused them to return to their original positions due to crystal growth and stress recovery. Fig. 4(f) provides the ionic conductivity measurement results for the as-deposited film;
these results were obtained using a DC 4-probe & the AC 2-probe method. The film showed an electrical conductivity of ~7.0 mS at 750°C. This value is lower than that of YSZ bulk ceramics; the discrepancy is probably due to the nano-sized grains and crystal defects that formed during the collision of particles. It is expected that the conductivity of the film will be enhanced by appropriate post-annealing.

For dense and defect-free electrolyte preparation, surface engineering of the anode support is important because thin film coatings tend to follow the structure of the surface material. As an anode material, NiO-GDC composite was used; various combinations of starting powders with different particle sizes and binder contents were tested, including NiO of Kojundo, Kceracell AFL grade, and GDC of Rhodia ULSA, FCM-m. Among those combination, Kceracell NiO and Rhodia GDC, mixed at a ratio of 6:4 and with a binder content of 50%, showed the best microstructure (Fig. 5). In the optimum conditions, it was possible to obtain an almost fully dense pore-free NiO-GDC AFL structure.

Figure 6 shows the cross-sectional full-cell microstructure
after cell-testing at 750°C, including the Ni-GDC-PMMA support, Ni-GDC AFL, YSZ electrolyte, and LSCF-PVDF cathode. The PMMA and PVDF polymer components, added as pore-formers, decomposed during cell fabrication and generated pores in the support and cathode, respectively, as shown in the figures. The microstructure clearly reveals a dense and porous structure both by coating process. The Ni-GDC anode consisted of a relatively dense, ~30 µm thick top functional layer on a porous, ~1.0 mm thick support. The thicknesses of the YSZ and LSCF coatings were ~5.3 and 25 µm, respectively. The surface microstructure of the deposited YSZ film showed dense structures with 50 ~ 100 nm surface roughness; the surface of the LSCF film showed a porous structure with a nano-sized pore structure.

Figure 7 shows the I-V and I-P curves for the full cell with different AFL structure. The surface of the AFL structure is also shown for comparison. As can be seen in the graph, the cell performances were strongly affected by the AFL structure. The cell showed higher OCV and maximum power density values when the electrolyte was deposited on the dense and optimized AFL structure. Under optimum conditions, the cell showed an OCV of 1.11 V, close to the theoretical value, and a maximum power density of approximately 1.3 W/cm² at 750°C, probably because the electrolyte deposited on the optimized AFL structure has a low gas leakage rate. Fig. 8 shows the cell stability test results under a con-
stant current condition of 200 mA, with the full cell including the YSZ and YSZ/GDC bi-layer electrolytes fabricated by the coating process. The cell showed almost no degradation up to 100 h at constant current condition if the reaction between LSCF and YSZ can be prevented by the GDC buffer layer.

4. Conclusions

An SOFC cell comprised of a YSZ electrolyte, Ni-GDC anode, and LSFC cathode was fabricated by a combination of conventional tape-casting, sintering, and novel ceramic thick film processes. The coating operating at room-temperature allowed us to successfully avoid an interface reaction between the components, and therefore the cell showed high performance, with a maximum power density higher than 1 W/cm² at 750°C; the cell also showed good stability due to the application of a GDC diffusion barrier layer between the YSZ electrolyte and the LSCF cathode. Anode-supported type SOFCs with high performance and good stability were fabricated using a coating process. The process is expected to be effective for the fabrication of next-generation high reliability metal-supported cells (MSC); study of MSC fabrication is under development.

Acknowledgments

This research was financially supported by the Fundamental Research Program of the Korean Institute of Materials Science (KIMS).

REFERENCES