

Fabrication of GDC-based micro tubular SOFC single cell using electrophoretic deposition process

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Micro tubular SOFC single cells with $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) electrolyte were fabricated by electrophoretic deposition (EPD) process. Stable slurries for the EPD process were produced by adding dispersant of phosphate ester to control the pH, conductivity, and zeta-potential. Anode support, an anode functional layer, and electrolytes were consecutively deposited and co-sintered on a graphite rod by an EPD process. The thickness of the deposited layer increased as the voltage amplitude and the deposition time increased. GDC-based micro tubular single cells with a 10 μm thick electrolyte showed a maximum power density of 0.42 W/cm² at 600 °C.

Key words: Solid oxide fuel cells, Micro tubular, Electrophoretic deposition, Slurry, Dispersant.

Introduction

Solid oxide fuel cells (SOFCs) are a well-known energy conversion technology that has attracted much attention due to their high-energy conversion efficiency and low pollutant emissions [1-3]. SOFCs can be categorized according to planar and tubular types based on their structural configuration. While planar type SOFCs have high current efficiency and power density, they need sealant to prevent air and fuel from mixing and are less reliable due to their poor heat cycle resistance [4, 5]. On the other hand, tubular-type SOFCs do not need sealant to connect cells. Tubular-type SOFC have shown stability and excellent performance over thousands hours [6, 7]. However, the lengthy current flow pass-way of the tubular-type SOFC increases the internal resistance of the cell, and consequently leads to a decrease in cell performance. Many researches on micro tubular SOFCs have been conducted to solve these problems. Micro tubular SOFCs are a highly efficient planar type and offer the structural stability of the tubular type due to an increase in reaction site versus volume. Moreover, with its small size, the micro tubular SOFC can be used as a portable device and performs better than batteries or any other fuel cell system. Micro tubular SOFCs have a thin multi-layer structure on one side of closed support. This structure is manufactured as follows: manufacture the porous anode tube, deposit thin dense electrolytes and deposit porous cathode on the electrolyte. However, conventional processes for thin film fabrication,

such as extrusion, tape casting, and spin coating, have disadvantage of high expense [8-10].

Meanwhile, electrophoretic deposition (EPD) is one of the most popular methods to fabricate thick films due to its simple apparatus, low cost, and fast processing time [11, 12]. Particles charged by charging agents are dispersed in a stable suspension. When a DC-electric field is applied, the charged particles move and are deposited on a support [13, 14]. In this study, dense GDC electrolyte films were fabricated on the porous NiO-GDC anode supports. Various processing conditions, such as amount of charging agent, applied voltage, and deposition time, have been investigated.

Experimental Procedure

The first step for the fabrication of micro tubular SOFC single cell by EPD process is to prepare stable slurry of anode support layer, anode functional layer (AFL), and electrolyte layer, respectively. Slurry for each layer was prepared with various compositions by ball-milling. The slurry of $\text{NiO-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) anode support layer (Ni:GDC = 60:40 vol%) was prepared by mixing NiO (FP, Smitomo) and GDC (UHSA, Rhodia) powders with 30 vol% of PMMA (SUNPMMA-S100, Sunjin chemical) as pore former in anhydrous ethanol (Aldrich). Phosphate ester (PE, ethyl acid phosphate, Johoku chemical) was also added as dispersant. After ball milling for 15 h, little more anhydrous ethanol was added and stirred in a beaker for 8 h. Finally, 5 wt% polyvinyl butyral (PVB, Aldrich) was added as a binder and then stirred for 8 h. The slurry of AFL has the same composition as the NiO-GDC anode support layer. However, pore former and binder were not used. Only PE was added to anhydrous ethanol and mixed by ball-

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milling for 8 h. GDC (UHSA, Rohdia) powder was used for the slurry of the electrolyte layer. After GDC powder, PE, and anhydrous ethanol were mixed by ball-milling for 15 h, 5 wt% PVB as a binder was added and then stirred for 8 h. These prepared stable slurries were deposited on a graphite rod with a constant current and various voltages and times. The deposited samples were dried for 24 h at room temperature and co-sintered at 1500 °C for 6 h. A leakage test for the sintered samples was carried out with an air pump and shrinkage tube in a water bath. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}\text{-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (LSCF-GDC 50 : 50 wt.%, Fuel cell materials) cathode paste was deposited by brushing it on. It was then dried for 24 h at room temperature followed by firing at 1100 °C for 2 h. Au was used as a current collector. Au paste was deposited on both the cathode and anode sides, and then fired at 800 °C for 1 h. Current-voltage (I-V) measurements of the single cells were performed using a fuel cell test station (SMART2, WonATech Co. Ltd, Korea) at 600-700 °C. Humidified H_2 (~3% H_2O at 30 °C) and dry air were supplied as a fuel and oxidant, respectively.

Results and Discussion

Characteristics of the slurry

pH, electrical conductivity, and zeta-potential of each slurry were measured with various amounts of PE in order to evaluate the stability of the slurry. PE is an effective dispersion agent, which can charge positively by providing the surface of a particle with protons. When organic solvent dissociates PE, the hydroxyl group combined with the phosphate releases the proton and the isolated protons are absorbed on the surface of the particle as a result of the interaction between the acid and the base. When the amount of PE increases, proton absorption becomes saturated, and the dissociation of PE reaches the equilibrium state. Consequently, the pH value decreases sharply and then becomes saturated. [15, 16]. On the other hand, electrical conductivity increases with increasing PE content due to an increase in the amount of protons. However, when the amount of absorbed protons is saturated, electrical conductivity is also fixed at a regular value. Since electrical conductivity affects the mobility of particles in the slurry, it is one of the important parameters during the EPD process. Meanwhile, when the value of the zeta-potential is higher than the isoelectric point, the particles are well dispersed.

As shown in Fig. 1, the pH of NiO-GDC anode support slurry rapidly decreased, and then was saturated when the pH value was less than two. Electrical conductivity gradually increased as the amount of PE increased. The zeta-potential showed the highest value of 18 mV at 1.5 wt% of PE and that indicates the most stable slurry. Although the highest conductivity is not achieved at 1.5 wt% of PE, this slurry may have enough driving force to move particles. Meanwhile, the proper amount

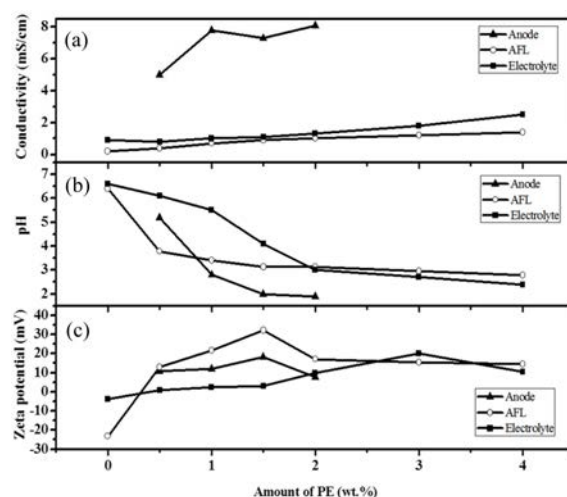


Fig. 1. (a) Conductivity, (b) pH, and (c) zeta-potential for NiO-GDC anode support, NiO-GDC AFL, and GDC electrolyte slurry, respectively, as a function of the PE concentration.

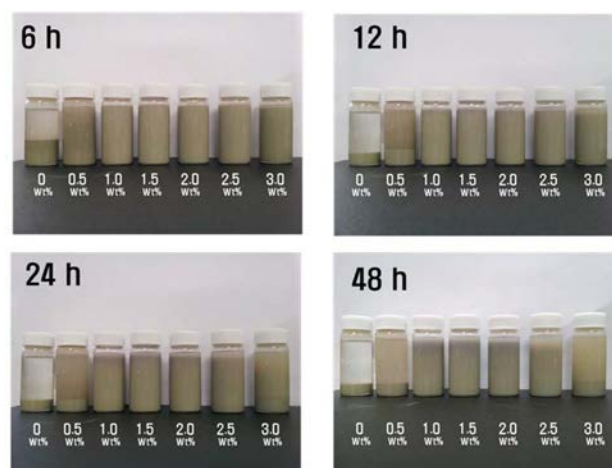


Fig. 2. Stability of NiO-GDC AFL slurry with time.

of poly(methyl methacrylate) (PMMA) as a pore former for NiO-GDC anode support was determined by measuring the porosity of reduced samples with PMMA. Samples with 20, 25, and 30 vol% of PMMA, respectively, were sintered at 1500 °C for 6 h followed by reducing in an H_2 atmosphere at 800 °C for 2 h. The measured porosity of the reduced samples with 20, 25, and 30 vol% of PMMA was 31.9%, 34.7% and 36.4%, respectively. In case of the AFL slurry, the pH value decreased but the electrical conductivity increased with an increasing amount of PE. The highest zeta-potential value of 30 mV was achieved at 1.5 wt% of PE. The GDC electrolyte slurry showed a similar trend. While electrical conductivity increased with increasing PE, the pH decreased. The highest zeta-potential value of 20 mV was obtained at 3 wt% of PE. Therefore, 3 wt% of PE was determined as the optimal condition of GDC electrolyte slurry for the EPD process.

The slurry stability with various amounts of PE was also evaluated using a precipitation test. The actual dispersion stability of the AFL slurry is shown in Fig. 2. The slurry without PE exhibited the layer separation

Table 1. Optimal slurry conditions for the EPD process.

Slurry	PE (wt%)	PVB (wt%)	PMMA (vol%)	Solid loading (solute: solvent)
NiO-GDC anode support	1.5	5	30	80 : 100
NiO-GDC AFL	1.5	-	-	14 : 100
GDC electrolyte	3	5	-	7 : 100

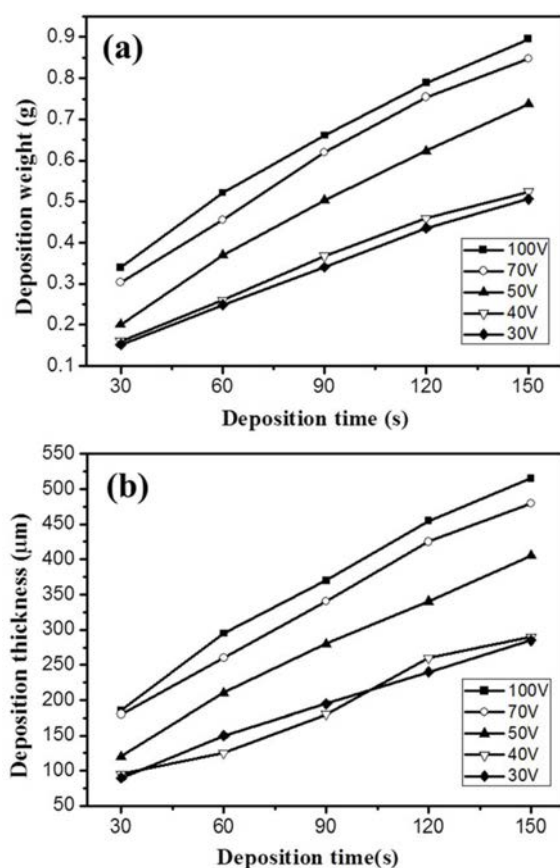
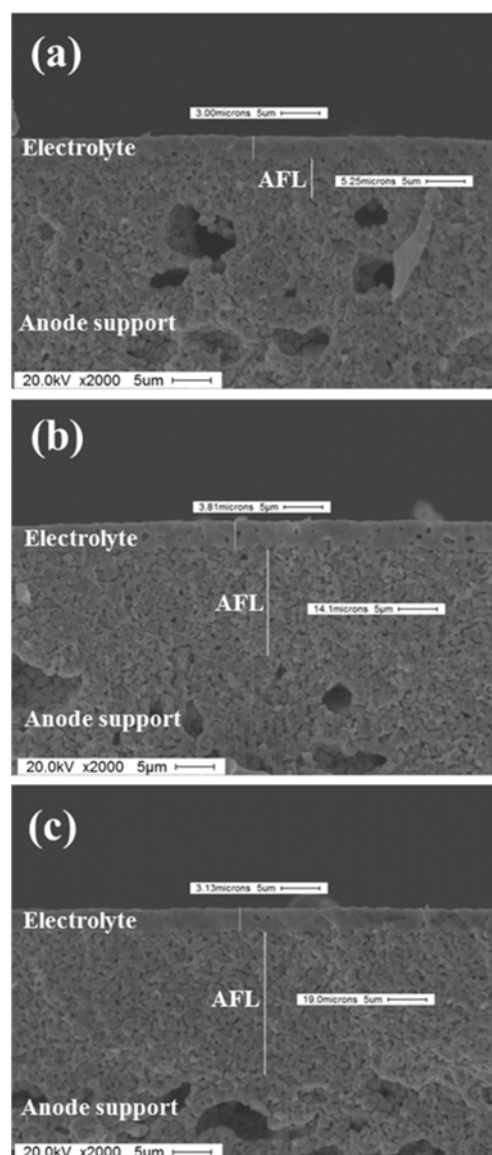
due to an agglomeration of powders in the slurry within 6 h and completely precipitated a day after. Interestingly, the samples that contained more than 2.5 wt% of PE also showed the precipitation after 48 h. The super-saturation of PE on the surface of particles may induce the precipitation. Accordingly, the optimal amount of PE for the preparation of a stable AFL slurry was confirmed as 1.5 wt%. This result is in accordance with the zeta-potential measurement as shown in Fig. 1. The optimal conditions for the slurry of the anode support, AFL, and electrolyte layers are listed in Table 1.

Deposition parameter control during EPD process

A well-dispersed stable slurry was deposited on the graphite rod by the EPD process. NiO-GDC anode

supports were deposited with various deposition times and voltages in order to evaluate the deposition weight and thickness. Fig. 3 shows the thickness and weight of the deposited green body samples dried for 24 h at room temperature. The deposition current was fixed at 20 mA. It was confirmed that both the deposition weight and thickness of the anode support increased when the deposition time and the voltage were increased. While both deposition weight and thickness increased linearly with the deposition time, there is no significant difference between those results at 30 V and 40 V. However, cracks were observed when a high voltage was applied. Particles move too fast at high voltages and this leads to the interruption of the close packing.

Fig. 4 shows the microstructure of the co-fired samples with various deposition times. The samples

**Fig. 3.** The deposition (a) weight and (b) thickness of the NiO-GDC anode support as a function of the deposition time and voltage.**Fig. 4.** Cross-sectional SEM images of the NiO-GDC AFL deposited in (a) 20 s, (b) 30 s, and (c) 40 s at 20 V and 20 mA.

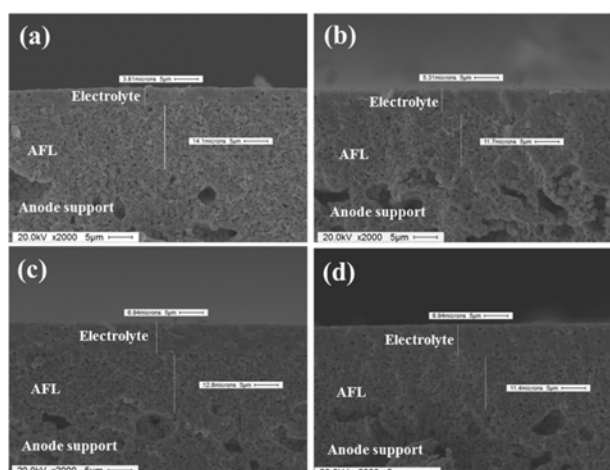


Fig. 5. Cross-sectional SEM images of the GDC electrolyte deposited with various parameters: (a) 20 V and 20 s, (b) 20 V and 30 s, (c) 20 V and 40 s, and (d) 30 V and 30 s.

Table 2. Optimal deposition conditions for the EPD process.

Layer	Voltage (V)	Current (mA)	Time (s)
NiO-GDC anode support	50	20	40
NiO-GDC AFL	20	20	20
GDC electrolyte	40	20	30

were co-sintered at 1500 °C followed by reducing at 800 °C in an H₂ atmosphere after deposition of the anode support, AFL, and electrolyte layer one after another. The thickness of the AFL layer increased when the deposition time increased at the same voltage and current (20 V, 20 mA) similar to the result shown in Fig. 3.

Similarly, the thickness of the GDC electrolyte layer gradually increased as the deposition time increased at the same voltage and current (20 V, 20 mA) as shown in Fig. 5(a), (b), and (c). At the same deposition time and current (30 s, 20 mA), the thickness also increased as the voltage increased (Fig. 5(b) and (d)). Interestingly, although the applied voltage and deposition time are different, the thickness is almost the same (Fig. 5(c) and (d)). This indicates that one can elaborately control the thickness and morphology of the thin or thick film by controlling deposition parameters, such as voltage and time.

Table 2 lists the optimal deposition conditions for the anode support, AFL, and electrolyte layers, respectively, in order to get crack-free rigid samples.

Electrochemical performance of the single cell

The picture and microstructure of the fabricated single micro tubular SOFC with a 2.5 mm diameter and length of 6 cm are shown in Fig. 6. The anode support, AFL, and electrolyte layers were deposited with the conditions as shown in Table 2. The LSCF cathode layer was deposited by a process of brushing followed

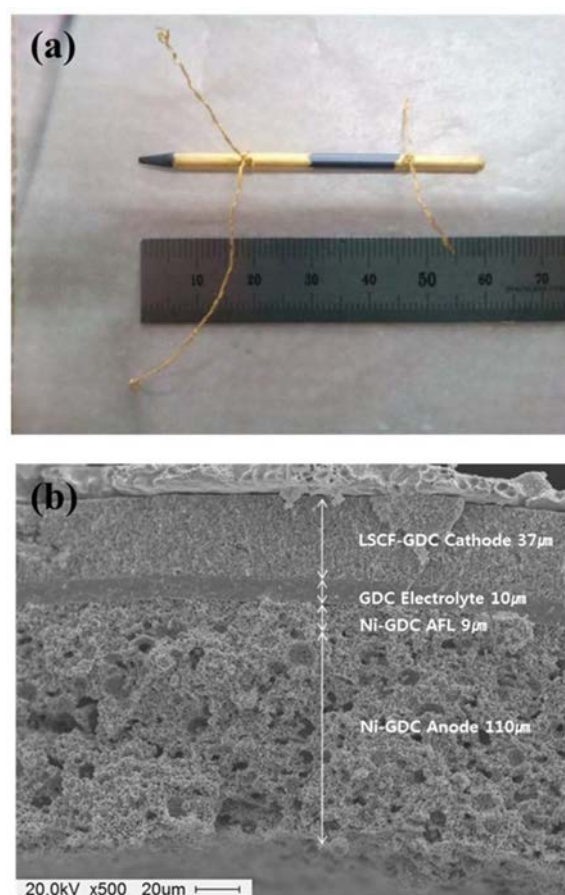


Fig. 6. The picture and cross-sectional SEM image of the micro tubular SOFC single cell that was fabricated.

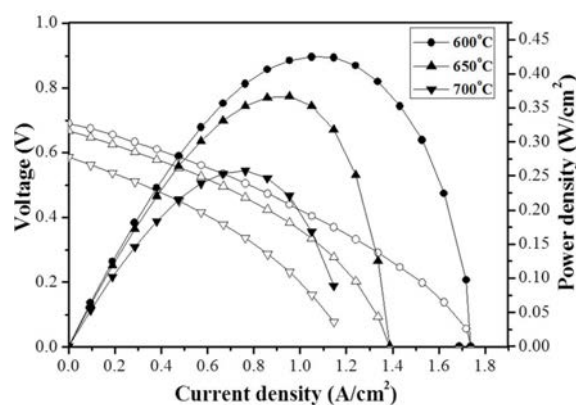


Fig. 7. Current-voltage (I-V) and power density curves for the GDC-based micro tubular SOFC single cells fabricated by the EPD process, measured at 600-700 °C.

by firing at 1100 °C for 2 h. All the layers were well attached without any delamination or cracks. The effective electrode area was 1.57 cm².

Single cell performance data at various operating temperatures are shown in Fig. 7. Generally, the open circuit voltage (OCV) of the GDC based-electrolyte was below 1.1 V due to the reduction of Ce⁴⁺ to Ce³⁺ at a reduced atmosphere. Considering the leak current, the OCV values of the micro tubular SOFC single cell that

was fabricated are relatively lower compared to the conventional GDC-based electrolyte. This might be due to gas leakage through the pin-holes on the 10 m thin electrolyte. Moreover, the power density decreased with an increase in the operating temperature, which is mainly caused by a reduction of OCV. Nevertheless, the micro tubular SOFC single cell exhibited considerable electrochemical performance. The maximum power density was 0.42 W/cm² at 600 °C.

Conclusions

The EPD process might be a promising technique for the fabrication of a micro tubular SOFC single cell, which has heterogeneous composites and a multi-layered structure because it is easy to control its thickness and deposition rate. PE was the effective dispersion agent which can positively charge the surface of particles. The thickness of the thin film increased as the deposition time and voltage increased. However, a non-uniform deposition layer formed when a high voltage was applied and the deposition time was long.

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