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Fabrication of La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ}-based micro-tubular SOFC single cells via electrophoretic deposition

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Micro-tubular solid oxide fuel cells with La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} (LSGM) electrolytes were fabricated by an electrophoretic deposition (EPD). Four layers of anode support, an anode functional layer, a buffer layer, and an electrolyte layer were successively deposited on a graphite rod via EPD, and the resulting architecture was subsequently sintered. The stability of slurries prepared for the EPD process was controlled by the pH, conductivity, and zeta potential. While the electrical conductivity of slurry increased with an increase in the amount of phosphate ester as a charging agent, the pH decreased. The thickness of the deposited layers increased with the applied voltage and deposition time. A micro-tubular SOFC single cell with the configuration of Ni-GDC anode support/Ni-GDC anode functional layer (AFL)/LDC buffer/LSGM electrolyte/ La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}-Ce_{0.9}Gd_{0.1}O_{1.95} (LSCF-GDC) cathode showed a maximum power density of 0.51 W/cm² at 800 °C.

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

Introduction

Solid oxide fuel cells (SOFCs) have been extensively studied as energy conversion devices due to their high energy conversion efficiency, environmental benignancy, and fuel flexibility [1-3]. SOFCs with oxygen ionconducting oxides as the electrolyte operate at high temperatures of 600-1000 °C so as to ensure sufficient oxygen ion conductivity in the oxide electrolyte. La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} (LSGM) electrolytes with a perovskite structure exhibit an ionic conductivity five times higher than that of state-of-the-art yttria-stabilized zirconia (YSZ) electrolytes at an intermediate temperature of 800 °C. Consequently, LSGM has been explored for use as an intermediate temperature electrolyte in SOFCs [4]. However, electrode selection is restricted with LSGM due to its reactivity with other components. In the case of Ni-YSZ, which is the most commonly used anode material in SOFCs, the YSZ reacts with LSGM and produces secondary phases such as La₂Zr₂O₇, Sr₂Zr₂O₄, and SrZrO₃. In addition, Ni reacts with LSGM and produces secondary phases of LaNiO₃ and La₂NiO₄. It has been reported that these secondary phases make the perovskite structure unstable. This in turn has a negative effect on performance and durability [5,6]. Moreover, LSGM reacts with ceria-based anode materials such as Ni-GDC (gadolinium-doped ceria) or Ni-SDC (samarium-doped ceria) so as to produce secondary phases of LaSrGa₃O₇ [7]. The formation of secondary phases is mainly due to La migration into ceria in the anode, leading to a deficiency of La in the LSGM [8]. Lanthanum-doped ceria (Ca_{0.6}La_{0.4}O₂₋₈, LDC) is generally used as a buffer layer to prevent La migration from LSGM [5]. For LSGM-based microtubular SOFC single cells, Ni-GDC anode support and functional layers can be utilized to obtain good electronic conductivity, high catalytic activity, and a sufficient triple phase boundary (TPB) at intermediate temperatures [9,10].

Electrophoretic deposition (EPD) is a particle movement control technology that uses electrons on the surface of a colloid in a dispersant (e.g., solution or organic solvent). The underlying phenomenon of EPD was discovered by GM. Bose in the 1740s [11-13]. EPD was first used by Harsanyi in 1927 to deposit tungsten and ThO₂ thin films with Pt anodes [14]. The EPD process is advantageous in that it allows for the rapid fabrication of uniform thick or thin films without the need for expensive equipment. Furthermore, the thickness and structure of films can be easily controlled [15]. The major parameters of EPD are the slurry and deposition conditions. The slurry consists of a solvent, a dispersion agent for slurry stability, a charging agent that charges the surface of neutral particles, and a binder that prevents cracking after deposition. With aqueous solvents, gases are readily evolved by electrolysis during the deposition process, resulting in the formation of pores in the thin film. Therefore, organic solvents are generally used in the EPD process [16]. In this study, micro-tubular SOFC single cells with the configuration Ni-GDC anode support/Ni-GDC anode functional layer (AFL)/ LDC buffer/LSGM electrolyte/La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃₋₆-

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 $Ce_{0.9}Gd_{0.1}O_{1.95}$ (LSCF-GDC) cathode were fabricated via EPD. The performance of the synthesized structures was subsequently evaluated.

Experimental Procedure

Slurries for the anode support and anode functional layers were prepared with 60 vol% of NiO (FP powder, Smitomo) and 40 vol% of GDC (UHSA, Rhodia). Phosphate ester (PE, butyl acid phosphate, $(C_4H_9O)_nP(O)(OH)_{3-n}$ n=1,2,Johoku Chem.) was used as both a charging and dispersion agent. Polymethylmethacrylate (PMMA, SUNPMMA-S100, Sunjin Chem.) was employed as a pore former to induce proper levels of porosity. Anhydrous ethanol was mixed with the above additives by ball milling for 15 hrs. A small amount of anhydrous ethanol was added into the mixed slurry and stirred for 8 hrs after adding polyvinyl butyral (PVB, Aldrich). The solid loading of the NiO-GDC anode support slurry was 81 of solute to 100 of solvent. In the case of the NiO-GDC AFL, binder was not added because no pore former was used. Anhydrous ethanol, PE, and the starting materials were mixed by ball milling for 15 hrs. The solid loading of the NiO-GDC AFL slurry was 15 of solute to 100 of solvent. In the case of the LDC buffer layer, LDC (LDC-F, Kceracell, Korea), PE, and anhydrous ethanol were mixed by ball milling for 15 hrs and then stirred for 8 hrs. The solid loading of the LDC buffer layer slurry was 6 of solute to 100 of solvent. For the LSGM electrolyte layer, LSGM powder (LSGM-P, Fuel Cell Materials), PE, and anhydrous ethanol were mixed by ball milling for 15 hrs and subsequently stirred for 8 hrs. PVB binder was then added, and the mixture was stirred again for 8 hrs. The solid loading of the LSGM electrolyte layer slurry was 7 of solute to 100 of solvent.

The NiO-GDC anode support layer, NiO-GDC anode functional layer, LDC buffer layer, and LSGM electrolyte layer were deposited in consecutive order on a graphite rod (Alfa Aesar, 3 mm diameter). The deposited green bodies were dried overnight and then co-sintered at 1450 °C for 6 h. A leak test was carried out to check for the presence of cracks after sintering. LSCF-GDC cathode paste prepared by a paste mixer was brushed on the sintered cells and dried overnight at room temperature. The dried samples were then sintered at 1100 °C for 2 hrs. Au paste was brushed on the sintered cathode and heated at 800 °C for 1 hr. Here, Au wire was used as a lead. Current-voltage (I-V) measurements of the single cells were performed at 500-700 °C using a fuel cell test station (SMART2, WonATech Co. Ltd, Korea). Humidified H₂ (~3% H₂O at 30 °C) and dry air were supplied as a fuel and oxidant at flow rates of 30 and 100 cm³/min, respectively.

Results and Discussion

Slurries for the NiO-GDC anode support layer, anode



Fig. 1. (a) Conductivity, (b) pH, and (c) zeta potential of NiO-GDC anode support, NiO-GDC AFL, LDC buffer, and LSGM electrolyte slurries as a function of the PE concentration.

functional layer, LDC buffer layer, and LSGM electrolyte layer were prepared with various amounts of PE. The electrical conductivity, pH, and zeta potential of each slurry were measured with different amounts of PE in order to evaluate the stability of the mixtures; the results are shown in Fig. 1. While the electrical conductivity was found to increase at higher PE amounts, the pH decreased. Dissociated PE molecules in the organic solvent have negatively charged O- sites and are combined with hydroxyl groups, thereby releasing protons. The isolated protons are absorbed on the surfaces of particles. Therefore, the electrical conductivity increase and pH decrease with higher PE contents are due to an increase in the number of protons. Since the separated PE molecules coordinate with protonated positive sites on the surfaces of particles, the zeta potential increases with PE content due to an increase in repulsion between PE, which has long alkyl groups, and the particles. In terms of stability, when the value of the zeta potential is higher than the isoelectric point, the particles are well dispersed and stable in the slurry. Meanwhile, electrical conductivity is an important factor in the EPD process because it affects the mobility of particles in the slurry. As shown in Fig. 1, the pH of the NiO-GDC anode support slurry exhibited a sharp decrease at higher PE contents, eventually saturating at 1.5 wt% of PE. However, the zeta potential reached a maximum value of 35 mV at 2 wt% of PE. Therefore, the optimum amount of PE for a stable NiO-GDC anode support slurry was confirmed to be 2 wt% of PE. While the NiO-GDC AFL slurry showed the same trends as the NiO-GDC anode support up to 2 wt% PE (i.e., an electrical conductivity increase and pH decrease at higher PE amounts), the zeta potential of the former reached a maximum of 28 mV at 1.5 wt% of PE. Therefore, 1.5 wt% was determined to be the optimal PE concentration for a stable and well-dispersed NiO-

Table 1. Optimal slurry conditions for the EPD process.

Slurry	PE (wt%)	PVB (wt%)	PMMA (vol%)	Solid loading (solute: solvent)
NiO-GDC anode support	2	4	30	87:100
NiO-GDC AFL	1.5	-	-	15:100
LDC buffer	2.5	-	-	6:100
LSGM electrolyte	3	5	_	7:100



Fig. 2. Cross-sectional SEM images of the LSGM electrolyte deposited at times of (a) 20 s, (b) 30 s, (c) 40 s (20 V, 20 mA), and (d) 40 s (30 V, 20 mA).

GDC AFL slurry. In contrast to the above findings, the pH of the LDC buffer layer slurry decreased significantly at 0.5 wt% PE, increased at 1 wt%, and then decreased again at higher PE contents. Furthermore, the electrical conductivity of the LDC buffer layer rapidly increased from 2.5 wt% PE. While the zeta-potential of the LDC buffer layer slurry reached a maximum value at 1.5 wt% PE, 2.5 wt% was selected as the optimum PE amount so as to ensure sufficient electrical conductivity. The electrical conductivity of the LSGM electrolyte slurry also increased up to 2 wt% PE; similar values were obtained at higher PE contents. Meanwhile, the zeta potential rapidly increased up to 0.5 wt% PE, at which point it almost became saturated. Regardless, 3 wt% of PE was needed in the LSGM electrolyte slurry to ensure a high enough electrical conductivity for particle movement. The optimal slurry conditions for LSGMbased micro-tubular SOFC single cell preparation are summarized in Table 1.

Upon optimizing the PE content in the slurries, anode support layers, a functional layer, an LDC buffer layer, and an LSGM electrolyte layer were deposited in consecutive order on a graphite rod.

Fig. 2 shows the microstructure of co-fired samples deposited at various times and voltages. The specimens were co-sintered at $1450 \,^{\circ}$ C for 6 hrs in air. At the same voltage and current (20 V, 20 mA), the thickness



Fig. 3. (a) Cross-sectional SEM image of the micro-tubular SOFC single cell, (b) surface of the LSGM electrolyte, and (c) an enlarged micrograph of the single cell.

Table 2. Optimal deposition conditions for the EPD process.

Layer	Voltage (V)	Current (mA)	Time (s)
NiO-GDC anode support	60	20	50
NiO-GDC AFL	20	20	20
LDC buffer	20	20	20
LSGM electrolyte	40	20	50



Fig. 4. Current-voltage (I-V) and power density curves for the LSGM-based micro-tubular SOFC single cells fabricated by the EPD process; the measurements were conducted at 500-800 °C.

of the LSGM electrolyte layer increased as the deposition time was extended (Fig. 2(a-c)). As evident in Fig. 2(c) and (d), an increase in voltage also led to a thickness increase at the same deposition time and current (40 s, 20 mA). Such findings indicate that control of the thin film thickness can be achieved in the EPD process through proper adjustments to deposition parameters such as voltage and time.

The microstructure of a fabricated single micro-tubular SOFC with a 2.5 mm diameter and length of 6 cm is shown in Fig. 3. The optimal deposition conditions for rigid and crack-free anode support, AFL, buffer, and electrolyte layers are listed in Table 2. The LSCF-GDC cathode layer was deposited by a process of brushing followed by firing at 1100 °C for 2 hrs. All fabricated layers were well attached with no delamination or cracks.



Fig. 5. Thermal stability of the LSGM-based micro-tubular SOFC single cell.

In particular, the LSGM electrolyte was very dense without any pinholes. The effective electrode area was 1.57 cm^2 .

The cell voltages and power densities of a micro-tubular SOFC single cell with the configuration of Ni-GDC anode support/Ni-GDC anode functional layer (AFL)/LDC buffer/ 18 µm-thick LSGM electrolyte/La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃₋₈-Ce_{0.9} Gd_{0.1}O_{1.95} (LSCF-GDC) cathode at various operating temperatures are shown in Fig. 4. The open-circuit voltage value decreased as the operating temperature was raised. The maximum power density was 0.27 and 0.51 W/cm² at 500 and 800 °C, respectively. Such results represent a considerable enhancement in electrochemical performance when compared to that of conventional YSZ electrolyte-based single cells in the intermediate temperature range.

Thermal shock cycle test results are displayed in Fig. 5. In one thermal shock cycle, the single cell operating on a constant current load of 100 mA/cm² at 800 °C was abruptly cooled to 200 °C. After 20 cycles, the single cell showed no performance degradation.

Conclusions

In the fabrication of an LSGM-based micro-tubular SOFC single cell via EPD, PE was determined to be an effective dispersion agent that can positively charge the surface of particles. A complicated multi-layered structure was successfully produced by EPD, and it was found that the thickness of component layers could be controlled by adjusting the deposition time and voltage. Ultimately, the LSGM electrolyte-based micro-tubular SOFC fabricated by EPD exhibited considerable electrochemical performance at intermediate temperatures as well as good thermal shock stability.

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