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# Fabrication of an $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ electrolyte-based symmetrical microtubular SOFC single cell with $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ electrodes via electrophoretic deposition

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 $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$  electrolyte-based symmetrical microtubular solid oxide fuel cells (SOFCs) with  $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$  electrodes were fabricated via electrophoretic deposition (EPD). Multi-layers of the anode layer, a buffer layer, a cathode layer, and an electrolyte layer were successively deposited on a graphite rod via EPD. A single cell can be obtained via a one-step co-firing processing. The stability of the slurries can be controlled by changing the amount of phosphate ester (PE), which is added as a charging agent. The electrical conductivity of the slurry increased with increasing PE, while the pH decreased. The deposition rate and thickness of the deposited layers increased with the applied voltage and deposition time. The fabricated symmetrical microtubular SOFC single cell, with the configuration of  $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ -Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (SFM-GDC) cathode, showed a maximum power density of 116 mW/cm<sup>2</sup> at 600 °C.

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

## Introduction

Eco-friendly renewable energy has attracted a great deal of attention as an energy source to replace fossil fuels. In particular, solid oxide fuel cells (SOFCs) are well-known highly-efficient energy conversion devices due to their high operation temperatures. These high operation temperatures enable the use of inexpensive catalysts without Pt because of the high kinetics, and SOFCs can be combined with heat-generation systems to obtain increased efficiency [1-4]. Although high operating temperatures have many benefits, the durability of devices can be significantly reduced by thermal expansion, reactions between single-cell components, and instability in the redox atmosphere. The high manufacturing cost is also a problem. These drawbacks are significant obstacles that have limited the industrialization of SOFCs.

It is not necessary to seal tubular SOFCs because their dense electrolyte can act as a sealant. Moreover, miniaturization of tubular SOFCs can maximize their advantages due to their increased durability during fast cooling and heating cycles [5-7]. Meanwhile, the electrodes of SOFCs are usually distinguished into anodes and cathodes. These different types of electrodes typically need to be sintered by separate processes during SOFC single-cell fabrication. However, some electrode materials are stable in redox atmospheres and exhibit high electrical conductivity and catalyst activity in both oxidizing and reducing atmospheres [8-13]. These electrode materials are useful for creating single cells because they can reduce the number of processing steps, manufacturing costs, and risks related to redox atmospheres.

The electrophoretic deposition (EPD) process has been introduced to drastically reduce the number of manufacturing steps. EPD can deposit uncharged materials such as ceramics, polymers, and metals [14]. A dispersant helps enclose the surface of colloidal particles, which are influenced by an electric field [15]. Thus, by changing the applied voltage and deposition time, EPD can freely control the degree of deposition. This makes it very simple and fast to fabricate complex layers [16, 17]. Therefore, EPD is the most suitable process for industrial systems when fabricating microtubular SOFCs; additionally, mass production should be able to further reduce manufacturing costs.

In this study,  $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$  (SFM) was investigated as both the cathode and anode materials for SOFCs due to its remarkable electrical conductivity, good catalytic activity, and excellent redox stability in both reducing and oxidizing atmospheres [18-20].  $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM), which has about five times higher ionic conductivity than YSZ, was used as an electrolyte material. Two types of LSGM electrolyte-based symmetrical microtubular single cells with SFM electrodes were investigated in this study. One has SFM-LSGM composite electrodes and the other has SFM-Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (GDC) composite electrodes. Both types of single cells were

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deposited under optimized EPD conditions and sintered to fabricate microtubular SOFCs.

## **Experimental Procedure**

Sr<sub>2</sub>Fe<sub>1.5</sub>Mo<sub>0.5</sub>O<sub>6-δ</sub> (SFM) powder was synthesized by a sucrose-modified combustion method using sucrose and pectin as the fuel and catalyst for combustion, respectively [13]. This was mixed with GDC (UHSA, Rohdia) or LSGM (LSGM-P, Fuel Cell Materials) to make the electrode slurry. For stable slurry preparation, 0.5 wt% phosphate ester (PE, ethyl acid phosphate, Johoku Chemical) was used as a dispersant. The slurry of the electrode layer contains PMMA (SUNPMMA-S100, Sunjin Chemical) as a pore former, polyvinyl butyral (PVB, Aldrich) as a binder, and anhydrous ethanol as an organic solvent. The slurries of the electrolyte and buffer layer were prepared by mixing the powders, PVB, and anhydrous ethanol without a pore former. All components of each slurry were thoroughly mixed by ball-milling for 15 hrs. The prepared stable slurries for the SFM-GDC (or SFM-LSGM) anode layer, LSGM electrolyte layer, and SFM-GDC (or SFM-LSGM) cathode layer were deposited one after another on a graphite rod (Alfa Aesar, graphite rod, 3-mm diameter) with a constant current and various voltages and times. The asdeposited green bodies were sintered at 1300 °C for 5 hrs. After leak testing, the single cell (with a current collector) was applied on the electrode. Au was used as a current collector. Au paste was deposited on both the cathode and anode sides, and the device was fired at 800 °C for 1 hr. Current-voltage (I-V) measurements of the single cells were performed using a fuel cell test station (SMART2, WonATech Co. Ltd, Korea) at 600 °C. Humidified H<sub>2</sub> (~3% H<sub>2</sub>O at 30 °C) and dry air were supplied as a fuel and oxidant, respectively.

#### **Results and Discussion**

Slurries for the SFM-GDC electrode layer, SFM-LSGM electrode layer, SFM buffer layer, and LSGM electrolyte layer were prepared with various amounts of PE as a dispersion agent. The electrical conductivity and pH of each slurry were measured with different amounts of PE in order to evaluate the stability of the mixtures. As shown in Fig. 1, the electrical conductivity increases as the amount of PE increases. When PE is dissolved in an organic solvent, the hydroxyl group combined with the dissociated phosphate releases protons, and these isolated protons are absorbed onto the surface of the particle. Therefore, the electrical conductivity increases with increasing PE due to an increase in the number of protons. Alternatively, when proton absorption becomes saturated and the dissociation of PE reaches the equilibrium state, the pH value decreases sharply and becomes saturated [21, 22].



**Fig. 1.** Conductivity and pH of the SFM-GDC electrode layer, SFM-LSGM electrode layer, SFM buffer layer, and LSGM electrolyte layer slurries as a function of the PE concentration.

Table 1. Optimal slurry conditions for the EPD process.

Slurry	PE (wt%)	PVB (wt%)	PMMA (vol%)	Solid loading (solute: solvent)
SFM-GDC	0.5	2.5	10	28:100
SFM-LSGM	0.5	2.5	20	28:100
SFM buffer	0.5	2.5	_	20:100
LSGM electrolyte	0.5	2.5	_	20:100

The overall optimal conditions for the SFM-GDC electrode layer, SFM-LSGM electrode layer, SFM buffer layer, and LSGM electrolyte layer are listed in Table 1.

Stable slurries were consecutively deposited on a graphite rod using the EPD process in the order of: anode support layers, SFM buffer layer, LSGM electrolyte layer, and cathode layer. The thickness of the optimized single cell was determined by the characteristics of each layer. In particular, the anode is thicker than the other layers because it is used as the supporting layer of the tubular single cell. As reported earlier [23-25], both the deposition weight and thickness of each layer increased as the deposition time and voltage were increased. Table 2 shows the optimal deposition conditions for the anode support, buffer, electrolyte, and cathode layers, respectively, that were used to obtain crack-free rigid samples.

The relatively fast and large shrinkage of SFM, relative to LSGM, can accelerate the sintering of the LSGM electrolyte. This effect allowed LSGM to be densely sintered, even at 1300 °C, as shown in Fig. 2. Generally, a temperature over 1450 °C is needed to

 Table 2. Optimal deposition conditions for the EPD process.

Layer	Voltage (V)	Current (mA)	Time (s)
SFM-GDC anode	40	20	60
SFM buffer	20	20	5
LSGM electrolyte	20	20	20
SFM-GDC cathode	20	20	20



Fig. 2. Cross-sectional SEM images of the SFM//LSGM//SFM multi-layers sintered at (a) 1300 °C, (b) 1350 °C, and (c) 1400 °C.

obtain a fully-dense LSGM electrolyte. At 1300 °C, the pores are well formed in the electrode, whereas the pores are blocked at 1350 °C due to the melting of SFM. Therefore, the sintering temperature of all single cells using SFM-based electrodes was fixed at 1300 °C.

The microstructures of the fabricated single cells sintered at 1300 °C are shown in Fig. 3. The microstructures of single cells with SFM-GDC electrodes and SFM-LSGM electrodes are distinctly different. Particularly, the pore size and porosity of the single cell with SFM-GDC electrodes are significantly larger than those with SFM-



**Fig. 3.** Cross-sectional SEM image of the symmetrical micro tubular SOFC single cells with (a) SFM-GDC and (b) SFM-LSGM electrodes.



**Fig. 4.** Current-voltage (I-V) and power density curves for the LSGM electrolyte-based symmetrical micro tubular SOFC single cells fabricated by the EPD process, measured at 600 °C.

LSGM electrodes. This may be due to the better sinterability of LSGM relative to GDC. Alternatively, the single cell with SFM-LSGM has a much denser electrolyte layer than the single cell with SFM-GDC. In order to obtain a high open circuit voltage (OCV) and prevent cross-leakage of gas, the electrolyte layer should be fully dense. However, the electrode layer should have enough porosity to provide proper gas diffusion. Therefore, the trade-off between the electrolyte density and the porous electrode microstructure should be considered. The cell voltages and power densities of symmetrical microtubular SOFC single cells with SFM-GDC electrodes and SFM-LSGM electrodes at 600°C are shown in Fig. 4. Although the single cell with SFM-LSGM electrodes has a dense electrolyte, as shown in Fig. 3, it exhibits a very low OCV due to the microcracks caused by rapid shrinkage. Alternatively, the maximum power density of the symmetrical microtubular SOFC single cell with SFM-GDC electrodes was 116 mW/cm<sup>2</sup> at 600 °C, which indicates superior electrochemical performance compared to that of conventional YSZ electrolyte-based single cells.

### Conclusions

Green bodies of multi-layered microtubular SOFC single cells can be easily prepared by the EPD process within 5 min. The microstructure, including the pore distribution and thickness, of each layer can be precisely controlled by changing the composition of the slurry and the deposition conditions. Therefore, the EPD process represents be a promising technique for the fabrication of microtubular SOFC single cells. Moreover, while conventional SOFC single cells should fire the anode and cathode separately, due to their significantly different sintering temperatures, a symmetrical SOFC single cell can be co-fired only once. The LSGM electrolyte-based symmetrical microtubular SOFC single cell with SFM electrodes, fabricated using the EPD process, exhibited considerable electrochemical performance at intermediate temperatures.

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