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Fabrication of thin films on an anode support with surface modification for high-efficiency intermediate-temperature solid oxide fuel cells via a dip-coating method

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ABSTRACT

We studied the surface morphology of a modified anode structure that is capable of increasing the triple phase boundary (TPB) and the effect of its morphological feature on the electrochemical performances. The top surface area of the anode functional layer (AFL) was increased to extend the TPB length and the high contact area between the electrolyte and the AFL. To increase the top surface area of the AFL, carbon particles, which have a particle size larger than 10 μm, were mixed with the AFL slurry solution and coated on the anode support layer. Carbon particles were burned-out prior to coating the electrolyte layer on the AFL. As a result, the electrolyte could be successfully coated on the top of the AFL, which has a rough morphology. Enhanced roughness of the top surface of the AFL via the modification process was verified through atomic force microscopy (AFM) analysis. In addition, the microstructures of the contact area between the AFL and electrolyte were studied through the use of scanning electron microscopy (SEM). The Solid Oxide fuel cell (SOFC)with a modified AFL displayed excellent performance in power density and electrochemical impedance spectroscopy (EIS), in comparison with a cell that had a normal AFL. Additionally, the cell with a modified AFL exhibited a 74% higher peak power density value than the cell with a flat AFL and displayed the lowest resistance value in EIS results.

1. Introduction

The solid oxide fuel cell (SOFC) is one of the most promising green energy harvesting systems due to its low pollutant emissions, high conversion efficiency and ability to utilize various types of fuel such as hydrogen, methane and natural gas [1–7].

Manufacturing the entire SOFC cell is complex since it requires many processes to be performed during cell fabrication, which results in its low productivity in industrial use [8]. In addition, the fabrication of the thin film for the anode functional layer (AFL) or electrolyte requires elaborate techniques that could prevent the de-lamination of layers and crack during the sintering procedure or cell operation [9]. For several decades, many studies have been carried out to find the most efficient method for thin film coatings, which focused on using tape-casting, screen printing, slurry spin-coating and sol-gel [10–13]. Among them, dip-coating has been considered the most adequate method for use in mass production because of the cost-effectiveness and simple procedure [12,14]. Dip-coating displays outstanding contact quality between the thin-film layer and the anode support layer (ASL), which leads to limited de-lamination failure of the thin-film layer after sintering the cell [15].

The performance of an SOFC is primarily governed by the length of the triple-phase-boundaries (TPB). A TPB is defined as a site where an electrochemical reaction between gas phases, an electrolyte and an electrode occurs and is one of the major factors that determines cell efficiency [16–21]. A large interfacial area between the electrode and electrolyte could increase the TPB length in the cell. Many experiments have been conducted to increase the contact area for the purpose of extending the TPB length. One of the most efficient approaches is the modification of the electrode structure. For example, Kim et al. have reported the deposition of electrolyte materials on an inverse opal structure *via* atomic layer deposition (ALD) [21]. Yoon et al. have fabricated a vertical composite structure for the electrode and electrolyte through pulsed laser deposition (PLD) [22]. This research into the modification of the electrode structure resulted in the enhancement of the electrochemical performance. However, these methods, using vacuum deposition techniques, are high cost, complicated, relatively unproductive and difficult to scale up in

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order to mass produce the SOFC. To overcome this obstacle, a few studies have been carried out that used a simple coating method coupled with surface modification of the electrode [23–26].

Herein, we report a simple method to fabricate the surface modified AFL (modified-AFL) and electrolyte *via* a two-step dip-coating method. To increase the top surface area of the AFL, the AFL solution mixed with carbon particles is uniformly coated onto the anode support layer, and the carbon particles are then burned out at a high temperature, which leads to the formation of a rough morphology on the top of the AFL layer. The electrolyte is coated onto the modified-AFL layer through the dip-coating method, which enables the conformal coating of a solution on a non-flat surface. The rough surface provides a larger interfacial area between the anode and the electrolyte, which improves the electrochemical performance of the SOFC. The schematic illustration of the whole procedure and its corresponding pictures are shown in Fig. 1.

2. Experimental

2.1. Cell preparation

An anode support layer was fabricated by using a tape-casting method. CeO_2 (purity ≥ 99.95%, Lumi-m, Korea) and NiO powder (99%, Alfa Aesar, USA) were mixed in a weight ratio of 45:55. These were then dispersed in a solvent mixture that consisted of ethanol and toluene in a weight ratio of 1:1. Fish oil (Sigma Aldrich, USA) was added as a dispersant and the mixture was ball-milled for 24 h. After breaking up particle agglomeration for one day, butyl benzyl phthalate (BBP, s-160, Tape Casting Warehouse, USA) and polyvinyl butyral (PVB, B-79, Tape Casting Warehouse) were mixed for 24 h. The prepared ASL slurry was degassed in a vacuum chamber for 8 h. After removing the air in the slurry, it was tape-casted by using a tape-caster (HTC-S1000, Han-tech, Korea). The tape was dried to remove the remaining solvent at 200 °C, and cut into $6.5 \times 6.5\ cm^2$-sized tape for use in the $5 \times 5\ cm^2$-sized cell. Subsequently, pre-sintering at 850 °C was performed.

2.2. Surface modified AFL

To fabricate the modified-AFL, a colloidal solution mixed with carbon particles was used. In the AFL colloidal solution, the weight ratio of NiO ($SSA = 8.539\ m^2\ g^{-1}$, K-ceracell, Korea) powder to GDC ($SSA = 10.270\ m^2\ g^{-1}$, K-ceracell, Korea) powder to carbon particles was 1:1:0.225 and the volumetric ratio among the particles in the AFL was 26%. The particles were dispersed in ethanol that had a weight ratio three times higher than the particles. The solution was then mixed with an appropriate amount of binder solution (K-ceracell, Korea), BBP, PVB and fish oil. A pre-sintered ASL was dipped into the AFL colloidal solution, left for 3 min and then raised at a speed of $0.17\ cm\ s^{-1}$. A polymer film was attached to the rear side of the ASL before it was dipped into the solution to prevent coating on the rear side. The carbon particles in the AFL and polymer film were then burned out by annealing them at 800 °C for 2 h in air. After the burn-out process, an electrolyte layer was coated onto the AFL with the same method. The ASL, with modified-AFL, was dipped in the electrolyte solution 3 times to generate adequate thickness of the electrolyte layer. To form the dense electrolyte layer, the electrolyte layer coated substrate was sintered at 1450 °C for 4 h in air.

For the cathode component, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ ($SSA = 8.831\ m^2$, K-ceracell, Korea) and $Gd_{0.1}Ce_{0.9}O_{1.95}$ ($SSA = 10.270\ m^2\ g^{-1}$, K-ceracell, Korea) powder were mixed with a binder solution using a paste mixer (HPM-500, Han-tech, Korea). The mass ratio of the two powders was 1:1. The cathode paste was screen printed onto the electrolyte and then fired at 1050 °C for 2 h in air. $La_{0.6}Sr_{0.4}CoO_3$ ($SSA = 9.554\ m^2$, K-ceracell, Korea) was used as a current collector and screen printed onto the cathode.

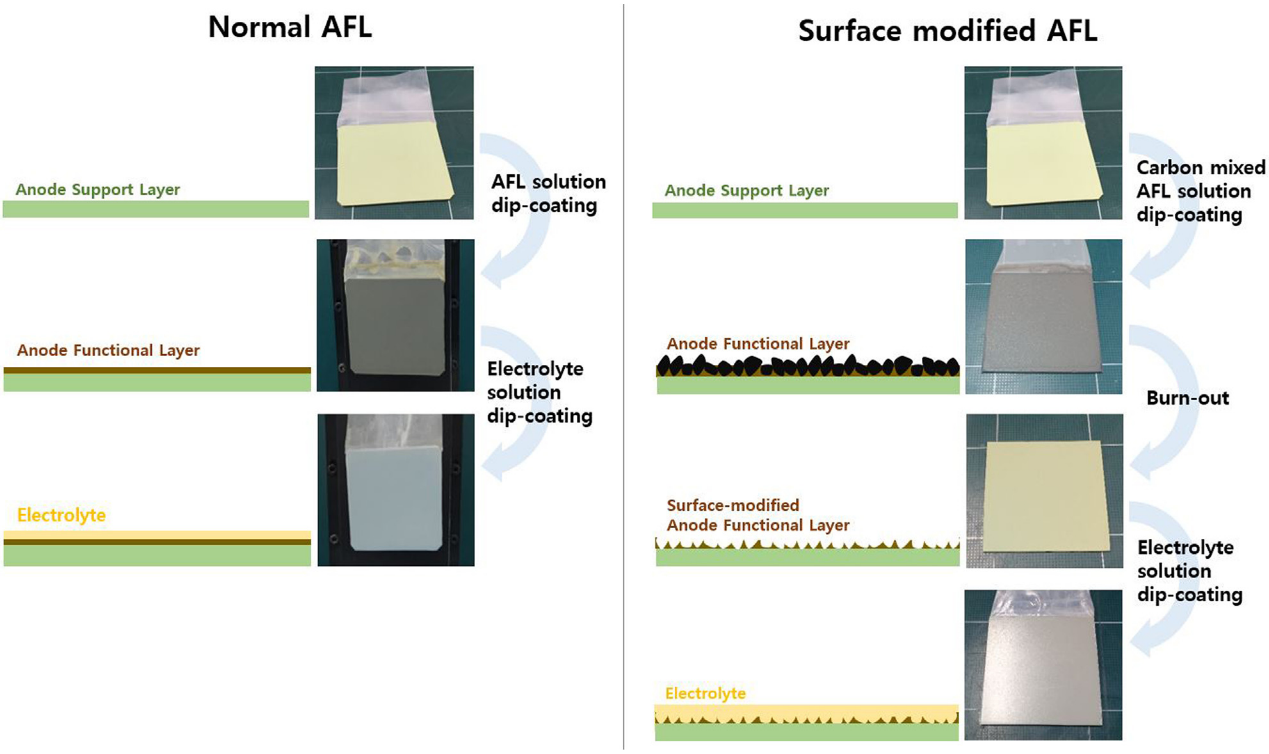

Fig. 1. Schematic illustration of the procedure of fabricating surface modified solid oxide fuel cells by using a natural carbon particle and its corresponding picture of the process.