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Electrochemical properties of electrospinning-fabricated layered perovskite used in cathode materials for a low temperature-operating solid oxide fuel cell

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ABSTRACT

In this study, the microstructural and electrochemical properties of linear type nanofibers obtained by adding $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SBSCO) layered perovskite oxide were investigated for use as cathode materials in a low temperature-operating solid oxide fuel cell.

Linear type SBSCO fiber and $Ce_{0.9}Gd_{0.1}O_{2-d}$ coated SBSCO-fiber were fabricated using the electrospinning process. It was confirmed that the area specific resistance (0.75 Ω cm^2) of the obtained SBSCO-fiber cathode was much lower than that (1.25 Ω cm^2) of a powder-type SBSCO cathode at 550 °C. The result shows that the SBSCO fiber cathode exhibits lower polarization resistance in low temperature ranges than the powder SBSCO cathode materials do. A significantly lower activation energy (0.76 eV) was observed in fiber SBSCO cathode than in the nanostructured $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-d}$ ones which were used as control at 1.53 eV.

1. Introduction

Most of researches on cathode materials for solid oxide fuel cells (SOFCs) have been devoted to perovskite oxides because a major portion of the voltage losses in SOFCs is caused by cathode overpotential [1].

To lower the overpotential of cathodes and improve the SOFC performances, advanced oxide materials can be used to obtain the electronic/ionic conductivity and enhanced catalytic activity for oxygen reduction. When it comes to the microstructure in cathodes, optimizing the cathode's microstructure help dramatically decrease its overpotential at the triple phase boundary (TPB), where the electrochemical reaction occurs.

For the fabrication of cathode materials, the most common and typical cathode preparation methods in the literatures include conventional powder mixing [2,3], sol-gel [4], and co-precipitation [2,5]. However, with these fabrication methods, it is not only difficult to control the TPB sites where the chemical reaction occurs for oxygen reduction at the cathode surface, but also the chemical reactions could be limited to the interfaces between the cathode and electrolyte and not extend over the entire interfaces. Therefore, various strategies have been applied to increase extensively the TPB sites in cathode materials used for SOFC. The electrospinning technique is one of them and has recently been adopted due to nanofibers made by electrospinning which are characterized by nanometer thickness, as well as their excellent porosity and surface control [6–9].

Recently, $La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_3$ (y = 0.2–1.0) fibers were obtained by electrospinning in order to extensively employ and expand the number of TPB sites of cathode materials [10]. For the direct application of cathode materials for SOFC, area specific resistance (ASR) of the composite cathode which comprises nanostructured $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-d}$ and ceria-based nanoparticles were

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characterized: the ASR values were 4.70, 1.12, 0.27, and 0.07 Ω cm^2 at 500, 550, 600, and 650 °C [11] respectively.

Our group reported that Sr-doped layered perovskite oxide systems, $LnBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (Ln = Pr, Sm, and Gd), exhibited excellent ASRs for an intermediate temperature-operating solid oxide fuel cell (IT-SOFC) cathode applications [12]. In the previous experiment, conventional powder mixing was used. The cathodic polarization of single phase and composite cathodes with 10 mol% gadolinia-doped ceria ($Ce_{0.9}Gd_{0.1}O_{2-d}$, CGO91) showed that a weight ratio between that of $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SBSCO) and CGO91 (i.e., 1:1, 50 wt% SBSCO and 50 wt% CGO91, or SBSCO:50) provided the lowest ASR of 0.10 Ω cm^2 at 600 °C and 0.013 Ω cm^2 at 700 °C [13] respectively.

Regarding the application of low temperature-operating solid oxide fuel cells (LT-SOFCs) as a cathode, previous studies published the results that nanofiber fabrication parameters were controlled to allow SBSCO to be carried using electrospinning. From this, the optimal conditions to fabricate the nanofiber for SBSCO cathode which maintains a linear form were established, and the fabrication conditions to obtain the nanofiber for SBSCO with an optimal linear form were presented [14].

For the purpose of the paper the microstructural and electrochemical properties of fabricated linear nanofibers, which were obtained by adding SBSCO layered perovskite oxide to materials for use in a LT-SOFC, were investigated. The influences of fiber type and powder type SBSCO cathodes were analyzed and compared for direct application as cathode materials for the LT-SOFC.

2. Experimental details

2.1. Phase synthesis of SBSCO layered perovskite

Layered perovskite with the chemical composition, $SmBa_{0.5}Sr_{0.5}Co_2O_{5+d}$ (SBSCO), was synthesized by the general Pechini method [15]. Stoichiometric amounts of nitrate materials such as samarium nitrate ($Sm(NO_3)_3$-$6H_2O$, 99.9%, Alfa), barium nitrate ($Ba(NO_3)_2$, 99.95%, Alfa), strontium nitrate ($Sr(NO_3)_2$, 99.97%, Alfa), and cobalt nitrate ($Co(NO_3)_2$-$6H_2O$, 98.0–102.0%, Alfa) were precisely weighed with a metal-ion ratio of 1.0:0.5:0.5:2 and then dissolved in deionized water. In addition, citric acid (99.5%, Alfa) and ethylene glycol (99%, Alfa) were added to the nitrate solution for the sol (colloidal solution) processing. Sol containing nitrates was prepared by adjusting the solution to pH 7 using ammonia solution. The prepared sol was heated to 200 °C on a hot plate while stirring, and SBSCO gel was obtained after removing the deionized water. The SBSCO gel formed afterwards was further heated at 250 °C to carry out the first calcination; then the secondary calcination was carried out at 600 °C to form single phase SBSCO.

After about 0.5 g of powder was placed on a metal frame of 20 mm in length, 12 mm in width and 1.5 mm in thickness and the surface of the packed powders was maintained at the same height as the metal frame, X-ray diffraction (XRD) patterns of the prepared samples were obtained using a Philips X'pert Pro diffractometer using Cu radiation (λ = 0.15418 nm). The X-ray tube was operated at 40 kV and 40 mA. The data collected from 2θ = 10° to 90° were matched with the reference data for identification of the crystal structures.

2.2. Electrospinning process and fabrication of SBSCO fiber

Ethanol was used as the solvent for the SBSCO fiber (hereafter, SBSCO-F) fabrication. Polyvinylpyrrolidone (PVP, M.W. 1,300,000, Sigma-Aldrich), which has relatively a higher molecular weight, was selected and used as the solute because the length of the nanofibers differs depending on the molecular weight of the polymer used in the experiment.

The weights of PVP and ethanol were calculated and mixed at a weight ratio of 1:10 (4 g of PVA: 40 g of ethanol) with magnetic stirring at 40 °C for 2 h. Then, SBSCO powders (SBSCO-P) synthesized by the Pechini method were added to the polymer solution resulting in a solution containing stoichiometric SBSCO powders (SBSCO-P), PVP, and ethanol in a weight ratio of 1:1:10 and then stirred at a high speed (500 rpm) for 2 h.

The electrospinning system used to fabricate the fibers consists of a syringe with a capacity of 10 mL (model Norm-Ject, Henke-Sass Wolf), a syringe nozzle with 0.30 mm of outer diameter (30 G), a syringe pump (model Legato 100, KD Scientific), and a high-voltage power supply (Korea Switching, model B-140). The prepared solution was put in the syringe connected to the 30G nozzle. The positive pole was connected to the syringe nozzle that was connected to the syringe pump. The electrospinning process was performed by connecting the negative pole to the collecting plate. The feed rate of the syringe pump was set at 3.0 mL/h, and the working distance from the syringe nozzle to the collecting plate was 12 cm under an applied voltage of 12 kV when using the electrospinning process. A detailed experimental schematic is presented in the literature [14].

2.3. Fabrication of SBSCO core fiber and core cell

SBSCO core fiber (SBSCO-FC) was fabricated using SBSCO-F with gadolinium nitrate ($Gd(NO_3)_3$-$6H_2O$, 99.9%, Alfa) and cerium nitrate ($Ce(NO_3)_3$-$6H_2O$, 99.9%, Alfa). For example, the Pechini method was used to coat 10 mol% gadolinia-doped ceria ($Ce_{0.9}Gd_{0.1}O_{2-d}$, CGO91) particles onto SBSCO-F annealed at 550 °C. In detail, gadolinium nitrate and cerium nitrate were dissolved in deionized water at 1:9 M ratio, and sol was prepared after completion of mixing. SBSCO-F prepared by electrospinning was added to the prepared sol, and then stirred on a hot plate. Heat treatment was performed at 200 °C to evaporate water from the solution and obtain the gel. The first calcination of the prepared gel was carried out on a hot plate at 250 °C. After the first calcined powder was recovered, the second calcination was conducted in a furnace at 1000 °C to proceed with the single phase synthesis [16].

The SBSCO core cell (named SBSCO-PC in this experiment) was also fabricated. The SBSCO-P prepared by the Pechini method was coated with CGO91 to form the core cell.

2.4. Fabrication of SBSCO-CGO91 composite cathode

A composite cathode (SBSCO-Com) comprising SBSCO-P and CGO91 powder was also fabricated to measure its microstructure and electrochemical properties. To do this, 50 wt% of SBSCO powder and 50 wt% of CGO91 powder were mixed; then an additional 2 wt% of KD-1 (Imperial Chemical Industries PLC, England) was also added for efficient distribution of the particles of the composite cathode. Butvar powders were ground in a mortar and pestle. Vehicle systems comprising 95 wt% of α-Terpineol and 5 wt% of Butvar were mixed and then these mixtures were placed in an oven heated to 60 °C for 24 h, and the vehicles were cooled to room temperature afterwards. The process of fabricating the composite cathode paste is as follows. After accurately weighing 5 g of cathode materials and 2.5 g of vehicles, cathode materials and vehicles were place in a 100 mL glass beaker and mixed on a stirring plate for 72 h with acetone added for a uniform paste. In this process, 50 mL of acetone was used. When acetone was removed from the mixed solution after 72 h, a viscous paste was obtained. The fabricated paste was stored in screw cap vials (24 mL, SamwooKurex) to prevent contamination and drying due to ambient temperature. More detailed information and the initials designating the samples used in this experiment, are shown in Table 1.

2.5. Microstructure analysis and electrochemical characterization

The microstructures of cathode materials were investigated using field-emission scanning electron microscopy (SEM, S-4200, Hitachi) with an accelerating voltage of 20 kV.