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Fibrous mixed conducting cathode with embedded ionic conducting particles for solid oxide fuel cells

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ABSTRACT

The $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) fibers with embedded nano-$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) particles are fabricated by electrospinning process using commercial SDC nanopowders and an SSC precursor gel containing polyvinyl alcohol (PVA) and aqueous metal nitrate. After calcination at 800 °C, fibers with diameters ranged between 300 and 500 nm and well-developed SSC cubic-perovskite structure and SDC fluorite are successfully obtained. The calculated crystallite sizes of SSC and SDC are 20.78 and 45.35 nm, respectively. Over whole measured temperature ranges during the symmetrical cell test, the fiber composite cathode exhibits much lower polarization resistance than conventional powder composite cathodes. The polarization resistances are estimated to 0.06 and 1.23 Ω cm^2 for the fiber composites and 0.15 and 2.10 Ω cm^2 for the powder composites at 700 and 550 °C, respectively. The single cell with the fiber composite cathode shows much higher performances; its maximum power density is 380.5 mW cm^{-2} at 550 °C and higher than 1278 mW cm^{-2} at 700 °C.

1. Introduction

Current research in the field of Solid Oxide Fuel Cells (SOFCs) aims at lowering the operating temperature below 800 °C to overcome the problems caused by high temperature operation. However lowering the operating temperature inevitably decreases the rate of surface reactions and bulk diffusion in cathode, which deteriorates the performance of a single cell [1]. Consequently, surface exchange and ionic conduction must be improved to maximize the yield of the cathode reaction. This improvement could be realized by not only new material selection but also detailed control of microstructure [1–3]. Very recently, the beneficial effects of the fibrous cathode using mixed ionic and electronic conducting (MIEC) materials have been reported [3–8]. For the MIEC cathode materials, the oxygen reduction reaction (ORR) occurs over the entire surface, and the major electrical pathway is the entire volume [1,10]. When a fiber structure composed of nano-grains MIEC materials is applied to the cathode, it is expected to not only maximize the number of reaction sites which is comparable to that of the nanoparticles, but also minimize the interfacial resistance by improving the phase connectivity which ensures much faster transport of both electrons and oxygen ions [4–9]. In one instance, Zhi et al. reported that the nanofiber network cathode using MIEC

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materials is highly percolated and connected, which offers a "highway" for ion and electron transport [8].

Meanwhile MIEC materials have been widely used in composite cathodes mixed with oxygen ion conducting particles to enhance their electrochemical and mechanical properties [11]. Accordingly, continuous attempts to combine the MIEC fiber with the ion conducting particles have been made, aiming at increasing the ionic conducting path and the triple phase boundary (TPB) sites. Several types of the fibrous composite cathode have recently been reported to exhibit excellent performance, but these were mostly fabricated by infiltrating/impregnating the ionic conducting materials on the surface of MIEC fiber [4,8,9]. The infiltrating/impregnating technique is a time-consuming process because of repeated infiltration and sintering steps to obtain sufficient loading, and it is more of a surface coating method than technique for composite. Therefore, the realization of composite structure contained within a fiber precedes all other methods producing coating or partial mixing.

We propose a simple and easy approach that makes it possible to embed the ionic conducting particles into the MIEC fiber. In case of the particle embedded fiber structures, there have been many efforts to fabricate the polymer or ceramic fibers containing metal nanoparticles (e.g. Ag, Au, Pt and Si) for various applications [12–18]. However, to our knowledge, there is no attempt to prepare the ceramic fiber with ceramic particles for SOFC application. In this study, the $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) particles were embedded in the $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) fiber matrix, which is designed to strengthen the advantages of fibrous cathode; (i) suppressing the grain growth of the SSC matrix by dispersed SDC particles, (ii) relieving residual thermal stress within the fibers, (iii) maintaining the overall porosity without filling the network pores, and (iv) simplifying the composite processing compare to other process such as infiltration.

This paper reports on the fabrication process of SSC fibers with embedded SDC nanoparticles by electrospinning, and the morphological and structural characteristics of the produced fibers are discussed in terms of the suitability as a composite cathode for SOFCs. Also, we compare the electrochemical performance of the SSC–SDC fibrous composite with the conventional composite cathode composed of SSC powders and SDC nanoparticles.

2. Experimental

The SSC fibers with the embedded SDC nanoparticles (SSC:SDC = 70:30 by weight ratio) were fabricated by electrospinning process. SSC was synthesized by the conventional sol–gel process and $Sm(NO_3)_3 \cdot 6H_2O$ (Sigma–Aldrich, 99%), $Sr(NO_3)_2$ (Sigma–Aldrich, 99%) and $Co(NO_3)_3 \cdot 6H_2O$ (Sigma–Aldrich, 99%) were used as starting materials for SSC precursor solution. Stoichiometric amounts of 0.4 M metal salts were dissolved in distilled water, followed by the addition of 15 wt% PVA (ACROS ORGANICS, MW: 88,000). 30 wt% of nano-SDC (surface area >100 $m^2\ g^{-1}$, Fuel Cell Materials, USA) was dispersed in isopropyl alcohol (IPA) by ultrasonication for 3 h. The SDC suspension (agglomerate size below 200 nm after sonication) and SSC precursor gel were mixed and then stirred for 24 h. The mixture was electro-spinned with the applied voltage of 20 kV. The composite fibers were calcined at 800 °C for 30 min in air. The as-spun and calcined fibrous composites were examined with high resolution X-ray diffractometer (HR-XRD, Bruker), field emission scanning electron microscope (FE-SEM, HITACHI S-4300SE), and transmission electron microscopy (TEM, JEM-2100 F, JEOL).

To prepare the cathode symmetric cells, two type symmetric cells of the fibrous and powder composite cathode were prepared by electrostatic slurry spray deposition; (i) The fiber type cathode slurry was prepared by mixing the fibrous composite with IPA, toluene, and polyvinyl butyral (PVB), (ii) the 70SSC–30SDC powder composite was prepared by mixing commercial SSC in the size range of 200–700 nm (D50: 498 nm, Winnertech, Korea) and SDC nano powder (the same SDC used in fabricating the fiber). The cathode mixtures were deposited onto both sides of the GDC pellet and sintered at 1000 °C for 2 h.

To fabricate anode supported single cells, the slurry of GDC (GDC powder dispersed uniformly in IPA, toluene with PVB) was electrostatic sprayed onto the pre-pressed 60NiO–40GDC pellet and co-sintered at 1350 °C for 3 h. The fibrous and powder composite cathode layers were prepared in the same way as symmetrical cell. Electrochemical impedance spectroscopy (EIS) was carried out using Solartron 1287 and 1260 (Solartron, UK). The single cell performance was evaluated

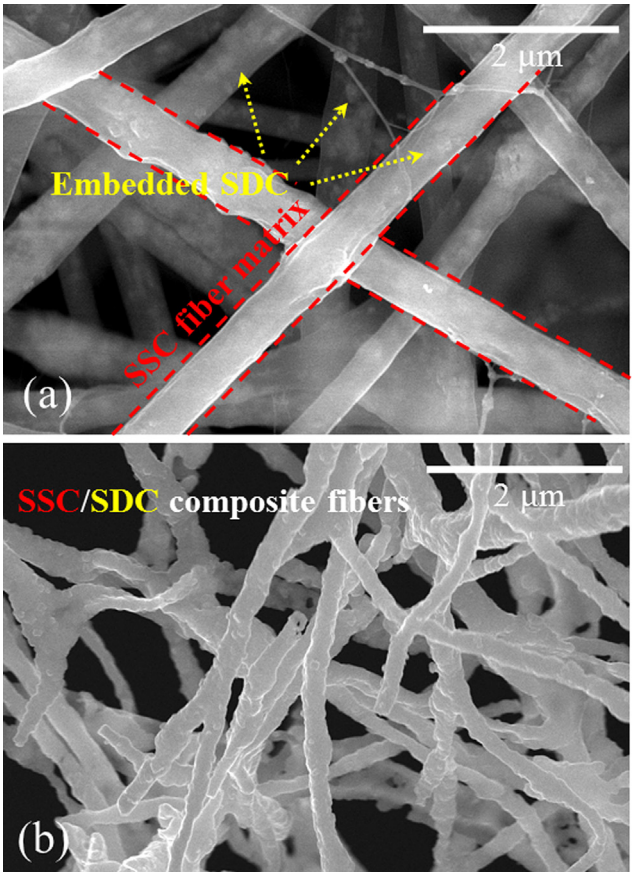

Fig. 1 – SEM images of (a) as-spun SSC fibers with embedded SDC nanoparticles, (b) after calcined SSC/SDC fibrous composite at 800 °C.

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