



# Stability of nanorod-structured $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ – $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ composite cathodes for intermediate temperature solid oxide fuel cells

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## Abstract

In this paper, the stability of the nanorod-structured  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF)– $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (GDC) composites prepared with combined methods of electrospinning and infiltration has been investigated. For comparison, conventional nanoparticle-structured LSCF–GDC composite cathodes were also developed. Electrochemical impedance spectra of these LSCF–GDC composite cathodes at open circuit potentials were measured using an electrolyte-supported LSCF–GDC/GDC/LSCF–GDC symmetric cell configuration for stability evaluation. The results show that the conventional LSCF–GDC composite cathode has poor stability, with its polarization resistance increasing from 0.80 to 1.37  $\Omega\text{ cm}^2$  after being polarized under a current density of 100  $\text{mA cm}^{-2}$  for 120 h at 650 °C. This degradation is attributed to the agglomeration of cathode materials and to poor contact between the cathode and the electrolyte. In contrast, the nanorod-structured LSCF–GDC composite cathode exhibits an excellent performance stability, since its polarization resistance decreases from 0.097 to 0.077  $\Omega\text{ cm}^2$  after polarization for 144 h under a current density as high as 300  $\text{mA cm}^{-2}$ . In addition, a nearly constant polarization resistance is maintained during a 20-cycle thermo-cyclic test. The outstanding stability of the nanorod-structured LSCF–GDC composite cathode is ascribed to the stability of its microstructure with continuous electronic and ionic conduction pathways and high porosity, this microstructure is realized through the suppression of LSCF agglomeration by the compact GDC layers. These results demonstrate that the nanorod-structured LSCF–GDC composite is a reliable material for use as intermediate temperature solid oxide fuel cell cathode with a high performance.

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## 1. Introduction

Solid oxide fuel cells (SOFCs) have been widely studied in the past several decades due to their high efficiency, low pollutant emissions and extensive fuel resources [1]. Recently, there has been considerable interest in developing low and intermediate temperature SOFCs (IT-SOFCs). Lowering the operation temperature not only reduces the production costs of SOFC components, but it also prolongs the cell lifetime. However, the SOFCs operated below 800 °C require high performance cathodes in order to maintain the desired cell performance.  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) is considered one of the most promising cathodes for IT-SOFCs due to its excellent balance of electronic and ionic conductivities as well as to the high electrocatalytic activity for

oxygen reduction reactions in the temperature range of 600–800 °C, and successful applications in IT-SOFCs have been reported [2–5].

Electrochemical performances of LSCF cathodes can be further enhanced by combining with ionic conduction phases to form composite cathodes [6,7]. Triple phases boundaries (TPB) are extended from limited sites along the cathode/electrolyte interface to active sites throughout the whole cathode. Among the methods for preparing composite cathodes, the wet impregnation method [8–10] is one of the most effective in obtaining high performance nanostructured electrodes due to the relatively low firing temperature. This method involves the decomposition and deposition of metal salts inside a pre-sintered porous electrode or electrolyte scaffold. Based on the wet impregnation method, high performance LSCF–GDC [11], LSCF–SDC [12] and LSCF–YSZ [13] composite cathodes were developed. Although these infiltrated cathodes

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showed lower polarization resistances as compared to the conventional composite cathodes, their long-term stability issues have not yet been properly addressed.

The LSCF-based cathode degradation commonly includes the following effects: (1) coarsening of cathode materials [14]; (2) chemical reaction between the cathode and the electrolyte, for example, the LSCF cathode reacts with the YSZ electrolyte to form the high resistance phase:  $\text{SrZrO}_3$  [15], and thus a rare earth doped ceria is usually introduced as an interlayer between the LSCF cathode and the YSZ electrolyte to avoid possible reaction between LSCF and YSZ [16–18]; (3) cathode delamination due to thermal expansion incompatibility between the cathode and the electrolyte; and (4) strong Sr segregation towards the surface of LSCF [19].

Recently, the degradation of infiltrated LSCF-based composite cathodes has been investigated. The stability of a LSCF infiltrated YSZ composite cathode [20] was evaluated at 750 °C using electrochemical impedance spectroscopy (EIS) under open circuit condition. The cathode polarization resistance changed from 0.17 to 0.3  $\Omega \text{ cm}^2$  after a 120-h load test, which was attributed to the microstructure evolution of LSCF nanoparticles in the composite cathode. In another article, the performance degradation of a LSCF infiltrated GDC composite cathode [21] was also investigated at 750 °C under open circuit condition. The result showed that the cathode polarization resistance increased from 0.3 to 0.83  $\Omega \text{ cm}^2$  after a 500-h test. The grain growth and coarsening of LSCF nanoparticles as well as the enrichment of Co on the cathode surface were considered to be responsible for the performance degradation of the composite cathode.

In our previous work, a one dimensional nanorod-structured LSCF–GDC composite cathode [22] has been successfully fabricated by combination of an electrospinning method with a multi-step infiltration method. The composite cathode exhibited excellent electrochemical performance, achieving the lowest polarization resistance of 0.1  $\Omega \text{ cm}^2$ . However, the stability of the one dimensional nanorod-structured LSCF/GDC composite cathode has not been investigated yet. Herein, the focus is placed on the long-term stability of the nanorod-structured LSCF–GDC composite cathode, which is evaluated with electrochemical impedance spectra measured within a period of operation under different current densities at 650 °C. In addition, a thermo-cyclic test of the composite cathode was performed between the temperatures of 300 °C and 650 °C to examine its thermal stability.

## 2. Experimental

Electrolyte pellets were prepared with GDC powders synthesized using a citrate complexation method [23]. The detailed fabricating process is described below. Stoichiometric amounts of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were dissolved in deionized water, and anhydrous citric acid was added. The solution was heated at 80 °C until a transparent gel was formed. The resultant gel was converted to a dry gel at 120 °C, which was further ground and calcined at 600 °C for 2 h to form GDC powders. Then, the as-obtained GDC

powders were die-pressed into discs, followed by sintering at 1450 °C for 20 h to form dense GDC electrolyte pellets with a size of 1.1 mm in thickness and 19 mm in diameter.

The LSCF cathode scaffolds were fabricated using nanorod-structured LSCF powders, which were synthesized by the electrospinning method [22]. The typical synthesis process is described below. Uniform and long LSCF precursor/PVP composite fibers were obtained by electrospinning of LSCF precursor solution consisting of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Polyvinylpyrrolidone (PVP) and N,N-dimethylformamide (DMF), and then sintered at 900 °C for 2 h with a heating rate of 2 °C/min, forming pure perovskite-type LSCF nanorods.

The electrolyte-supported symmetric LSCF–GDC/GDC/LSCF–GDC cells were then prepared using the nanorod-structured LSCF cathode materials. The nanorod-structured LSCF materials were mixed with 3 wt%-ethyl cellulose terpeneol solution, and coated on both sides of a GDC electrolyte pellet, and then sintered at 904 °C to form porous rod-structured LSCF cathode scaffolds with a geometric area of 0.7854  $\text{cm}^2$ . Then, a GDC phase was introduced into the LSCF cathode scaffold using a wet impregnation method. The GDC precursor solution for infiltration was prepared by dissolving stoichiometric  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in a mixed solvent of ethanol and deionized water. A microliter syringe was used to cast a proper amount of GDC precursor solution into the porous LSCF scaffold. To reach a sufficient amount of GDC, the impregnation process was repeated several times. Finally, the infiltrated LSCF scaffold was fired at 800 °C for 1 h in order to convert  $\text{Gd}(\text{NO}_3)_3$  and  $\text{Ce}(\text{NO}_3)_3$  into the GDC phase. The resultant LSCF–GDC composite cathode had a LSCF/GDC mass ratio of 1:1.

For comparison, a symmetric cell fabricated with two conventional nanoparticle-structured LSCF–GDC composite cathodes on both sides of a GDC pellet was also manufactured. The typical fabrication process was as follows. As-electrospun LSCF nanorods were pressed and ground into LSCF nanoparticles, and GDC nanopowders were synthesized using a glycine–nitrate process. Subsequently, a slurry consisting of LSCF nanoparticles and GDC nanopowders with a mass ratio of 1:1, as well as a proper amount of ethyl cellulose terpeneol solution, was dropped onto both sides of the GDC pellet, which was sintered at 950 °C in air for 2 h to form porous cathodes.

A Pt wire as the reference electrode was fixed at the rim of the GDC electrolyte disc using a Pt paste. Two Pt meshes as current collectors were attached to the symmetric LSCF–GDC composite cathodes. EIS were measured at the symmetric cells in air with one LSCF–GDC cathode as the working electrode using an electrochemical work station (Chi604D, Chenhua, China) with a frequency range of 0.1 Hz–100 kHz and a signal amplitude of 5 mV under open circuit condition. Different current loads were imposed on the LSCF–GDC composite cathode and the evolutions of EIS plots after galvanostatic polarizations were monitored to evaluate its long-term stability. The thermo-cyclic stability of the nanorod-structured LSCF–GDC composite cathode was also evaluated between

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