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Original Research Paper

LSCF–GDC composite particles for solid oxide fuel cells cathodes prepared by facile mechanical method

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ABSTRACT

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)–$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) composite is one of the most promising cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFC). However, currently most commonly used synthesis techniques for preparation of LSCF–GDC composite powders are very complicated and energy-consuming. In this study, a facile mechanical method to synthesize $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)–$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) composite powder was proposed. Such composite powder was formed by mechanical treatment of La_2O_3, $Sr(OH)_2$, Co_3O_4, Fe_2O_3, and GDC powders using a high-speed attrition-type mill. The results revealed that the LSCF–GDC composite powder was successfully synthesized through a short-duration (20 min) mechanical treatment, and the synthesized powder formed composite particles consisting of nano-sized particles. Furthermore, the resultant cathode after sintering at 900 °C exhibited very low polarization resistances of 0.08, 0.17, 0.38, and 0.69 $\Omega\,cm^2$ at temperatures of 800, 750, 700, and 650 °C, respectively.

1. Introduction

$La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (LSCF) compositions have attracted substantial interest owing to their superior mixed electronic–ionic conduction, which makes them promising cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFC) [1]. The electrical conductivity of the perovskite composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ can exceed 300 S/cm even at 600 °C [2]. However, a high activation enthalpy of 186 ± 5 kJ/mol for oxygen self-diffusion in LSCF has been reported [3]. Thus, the ionic conductivity drops rapidly with temperature. Enhancing ionic conductivity by adding an ionically conducting second phase, such as gadolinium-doped ceria (GDC), into LSCF to form a composite cathode would therefore be beneficial. The composite cathode would have a reduced polarization resistance compared to a pure LSCF cathode, especially at low temperatures [3–7]. For example, Leng et al. found that when 60 wt% $Gd_{0.1}Ce_{0.9}O_{1.95}$ was added to LSCF, the polarization resistance decreased by a factor of seven [4]. Murry et al. similarly discovered that the addition of 50 wt% $Gd_{0.2}Ce_{0.8}O_{1.9}$ to LSCF reduced polarization resistance by a factor of approximately ten [7].

Currently, the methods most commonly used to prepare LSCF–GDC composite powders require multiple steps. First, LSCF particles are synthesized by methods such as solid-state reactions [8], co-precipitation [9], hydrothermal synthesis [10], a sol–gel method [11], or a method involving the use of citrate [12]. Next, the surfaces of these particles are coated by fine particles of GDC through ball mixing. Although these methods provide high-quality LSCF–GDC composite powders, they have inherent disadvantages such as the high temperatures and/or long processing times required for synthesis, high production cost, and complexity. Thus, finding a simpler, energy-saving, and more easily scaled-up method to prepare fine composite powders is very important for SOFC materials research and their practical use.

Recently, we successfully demonstrated the short-duration synthesis of LSCF nano-sized particles without external heating, using a high-speed attrition-type mill [13]. The driving force for the synthesis was mechanical energy, applied through compression and shearing forces to the powder layer. This result suggests that both LSCF particle synthesis and its composite processing with fine GDC particles may be simultaneously possible using the attrition-type mill. This suggests a one-step process for LSCF–GDC composite particle creation, where fine particles of both LSCF and GDC are well dispersed.

In this paper, a facile mechanical process to synthesize LSCF–GDC composite particles was proposed, using the raw powder materials of LSCF and a fine powder of GDC. The properties of the synthesized powder were evaluated. Then, the cathode

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was fabricated by screen-printing the LSCF–GDC composite particles, followed by sintering. The electrochemical properties and microstructure of the resultant cathodes were evaluated.

2. Experimental

Fig. 1(a) shows the flow chart of mechanical processing to prepare LSCF/GDC composite particles in this method. As a comparison, a conventional method based on solid reaction is shown in Fig. 1(b). As shown in Fig. 1(a), the process in this method has only one step. For this experiment, the weight mixing ratio of composite powder was LSCF:GDC = 50:50. A high-speed attrition-type mill consisting of a stainless steel chamber and rotor was used to prepare the LSCF–GDC composite particles. The detailed configuration has been presented elsewhere [14]. First, commercially available La_2O_3 (average particle size, $d_{BET} = 300$ nm), $Sr(OH)_2$ ($d_{BET} = 750$ nm), Co_3O_4 ($d_{BET} = 23$ nm), and Fe_2O_3 ($d_{BET} = 34$ nm) with stoichiometric quantities (total amount = 70 g) were put into the chamber with one-fifth of the total amount of GDC powder ($Ce_{0.9}Gd_{0.1}O_{1.95}$, $d_{BET} = 24$ nm). Then, the powders were mechanically treated under air conditions without external heating. The rotor was driven by a motor (2.7 kW), and the maximum rotation speed was 4500 rpm. During mechanical processing, one-fifth of the total amount of GDC powder was added every 4 min. The total processing time was 20 min.

The crystalline phases were identified by powder X-ray diffraction (XRD, D2 phaser, Bruker, Germany) with Cu Kα radiation. The microstructure was characterized using scanning electron microscopy (SEM; ERA-8800FE, Elionix, Japan) and transmission electron microscopy (TEM; JEM-2010H, JEOL, Japan). The particle size distribution and its median size (D_{50}) were measured by the laser diffraction/scattering method (Microtrac MT3300EXII, NIKKISO, Japan). The specific surface area (S_{BET}) was determined by nitrogen gas adsorption based on the BET multipoint method (BET, ASAP-2010, Shimadzu, Japan). The mean BET-based size (d_{BET}) was estimated from the following equation: $d_{BET} = 6/(\rho \times S_{BET})$, where ρ is the theoretical density.

An electrolyte-supported cell was used for electrochemical performance testing. First, a fully dense GDC electrolyte, with a thickness of 600 μm and diameter of 15 mm, was prepared by uniaxial pressing of the GDC powder at 100 MPa, followed by sintering at 1350 °C for 2 h. The electrolyte substrate achieved a relative density of ~97%. The cathode was fabricated on one side of the electrolyte by screen-printing a paste of LSCF–GDC composite particles and polyethylene glycol, followed by sintering at 900–1200 °C for 2 h. The effective cathode area was 0.28 cm^2. The thickness of the cathode after the sintering was approximately 15 μm. A Pt paste was painted onto the other side of the GDC electrolyte substrate to serve as the counter and reference electrodes, followed by sintering at 850 °C for 1 h. A Pt mesh was used as the current collector for both the working and counter electrodes. The AC impedance of the LSCF–GDC composite cathode (half-cell) was measured with electrochemical impedance spectroscopy (EIS) in air at the temperature range of 650–800 °C. The EIS spectra were recorded using a frequency response analyzer with a potentiostat (Parstat 2263, Princeton Applied Research, TN, USA) in the frequency range 0.1–10^5 Hz with applied amplitude of 20 mV.

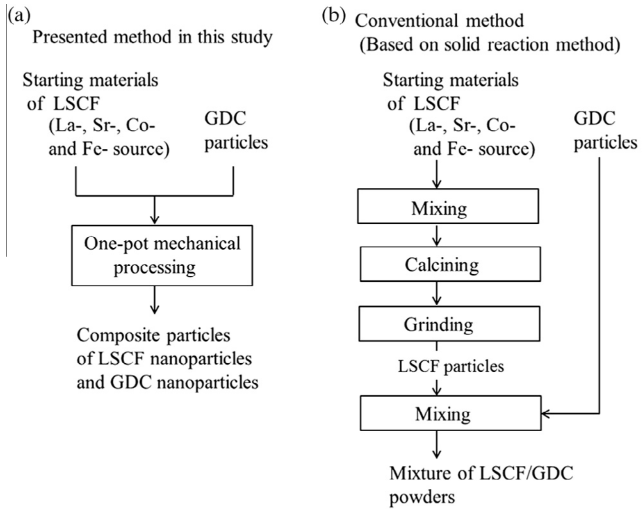

Fig. 1. Flow charts of the mechanical processing in this method and the conventional method.

3. Results and discussion

Fig. 2(a) shows the different XRD patterns of mechanically processed powders according to processing time. At 4 min, the main peak ($2\theta = 32.6°$) corresponding to the LSCF perovskite appeared. At 12 min, all peaks were corresponding to LSCF or ScSZ. The peaks corresponding to raw materials of LSCF disappeared. Therefore, it was supposed that the synthesis of LSCF was completed by 12 min processing. As a result, the XRD pattern of the composite

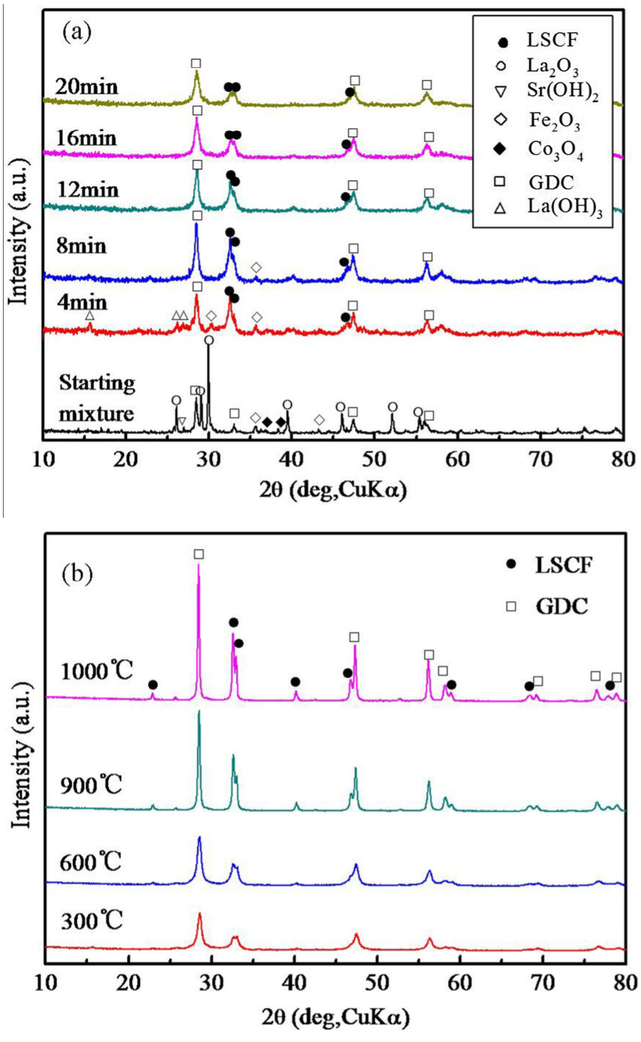

Fig. 2. (a) XRD patterns of the starting mixture and mechanically processed powders; and (b) XRD patterns of the composite powder after 20 min of processing fired at different temperatures.