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Characterization of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–$Ce_{0.8}Gd_{0.2}O_2$ composite cathode for intermediate temperature solid oxide fuel cells

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Abstract

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–$Ce_{0.8}Gd_{0.2}O_2$ (LSCF–GDC) composite cathodes with various weight ratios 90%, 70% and 50% of LSCF were prepared. Mechanical properties, thermal expansion properties and electrical properties were measured for potential applications in solid oxide fuel cells (SOFCs) with graded cathodes. LSCF and GDC as pure cathode and electrolyte materials were characterized as reference. The absence of new phases as confirmed by X-ray diffraction (XRD) analysis demonstrated the excellent compatibility between the cathode and electrolyte materials. Mechanical properties such as hardness and fracture toughness were measured by the micro-indentation technique, while hardness and elastic modulus were measured by the nano-indentation technique. Thermal expansion behavior was recorded by a dilatometer. Electrical conductivity was measured by the four probe DC method. The 50% LSCF–GDC composite has the lowest relative density among all the samples. Thermal expansion coefficients (TECs) and electrical conductivity increased with addition of LSCF contents in the composite, while mechanical properties depended more on the density than the LSCF content.

Keywords: B. Composites; C. Electrical conductivity; C. Thermal expansion; E. Fuel cells

1. Introduction

Intermediate temperature (IT, 500–800 °C) SOFC has gained a considerable attraction compared to a traditional high-temperature SOFC in that the reduced operation temperature allows low-cost metallic interconnects [1], helps to avoid material compatibility challenges at high temperature [2], reduces sealing and thermal degradation problems [3], and eventually accelerates the commercialization of SOFC technology. The overall cell performance, however, tends to decrease because of the reduced ionic conductivity of electrolyte and the increased polarization resistance of electrodes, especially on the cathode side [1]. Thus the development of higher-performance cathode is critical to overcome such technical barriers.

LSCF is one of the promising cathode materials for SOFC operated below 800 °C. Impedance spectroscopy data for LSCF electrodes have shown lower interfacial resistance than do conventional LSM electrodes [3]. The electrical conductivity of certain perovskite composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ can exceed 300 S/cm [4,5]. This composition is also attractive because the high Fe content yields a low thermal expansion coefficient than those of low Fe compositions, better matching the low TEC of the electrolyte. Unfortunately, LSCF cannot be used in conventional SOFCs because the LSCF perovskites are chemically incompatible with the YSZ electrolyte [6]. Fe or Co based cathode materials react readily with YSZ, forming high resistance phases $La_2Zr_2O_7$ and $SrZrO_3$ at the interface at high temperatures that deteriorate the cell performance [7,8]. The materials chemically compatible with Co-containing cathodes are doped ceria electrolytes, which possess a higher ionic conductivity than that of YSZ [9].

A commonly used method for improving the cathode performance is to add an ionically conducting second

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phase [10,11]. In the present work, $Ce_{0.8}Gd_{0.2}O_2$ was added to $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ to form a mixed conducting cathode of LSCF–GDC. The concept of functionally graded materials (FGMs) is also used to enhance the mechanical durability of the LSCF–GDC composite. The cathode in this study is designed with four layers consisting of 100% LSCF, 90% LSCF, 70% LSCF and 50% LSCF adjacent to the electrolyte GDC layer. General perspectives of material gradation have been described by Sasaki and Gauckler [12]. Instead of an abrupt change in composition and/or microstructure between the two materials, FGMs have a graded interface at which the composition gradually changes from one material to the other [13]. The difference with respect to physical properties of the cathode and electrolyte such as sharp discontinuities in TECs, which could result in delamination during thermal cycling, may be enhanced by allowing a gradual change in the composition between the two materials [14,15].

The objective of this study is to provide material properties of a graded LSCF–GDC cathode with various volume fractions of LSCF and GDC as materials database. The data for a dense cathode produced herein can be modified for the effective medium with realistic cathode porosities in an actual SOFC. In this regard, the present material properties can be the basis for predicting the thermo-mechanical behavior of the graded SOFC cell in operation environment (e.g. using finite element methods) which in general possesses enhanced mechanical durability (with lower probability of failure) and material compatibility compared to a typical layered SOFC.

The graded cathode is designed with four layers consisting of different LSCF contents adjacent to the electrolyte GDC layer. The LSCF–GDC pellets with four different compositions (100%, 90%, 70% and 50% LSCF) were prepared and characterized as each layer of the graded cathode. The electrical conductivity, thermal expansion and mechanical properties were measured with respect to the sintering temperature and the LSCF content.

2. Experiment

$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_x$ with a specific area 12.2 m^2/g was purchased from Seimi Chemical Corporation, and $Ce_{0.8}Gd_{0.2}O_2$ with a specific area 11.4 m^2/g was purchased from Daiichi Kigenso Kagaku Kogyo Corporation (DKKK) in Japan. LSCF–GDC cathode powders were prepared by ball milling LSCF and GDC powders for 24 h in ethanol to achieve good mixing. The weight percentage of LSCF in the mixing powders is 100%, 90%, 70%, 50% and 0%. After ball milling, the wet slurries were dried at 80 °C; then the dried powders were ground with a mortar and pestle and passed through 100 mesh sieves. The specific surface area of each powder after ball milling was determined through nitrogen adsorption based on the Brunauer–Emmett–Teller (BET) method [16] using a gas sorption analyzer (Nova 1000). The measured specific surface area was used to evaluate the properties of starting powders.

Monolithic pellets and rectangular bars were obtained by uniaxial pressing at 100 MPa and then sintered in air for 2 h with a heating rate of 2 °C/min. 100% LSCF samples were sintered at 1200 °C, 100% GDC samples were sintered at 1400 °C, and the composite samples were sintered at 1000, 1100 and 1200 °C. Phase characterization was determined by XRD analysis using Cu Kα radiation (Bruker D5005 advance X-ray diffractometer). The bulk density was determined by the Archimedes method with deionized water as the immersing medium. Basically specimens were saturated by boiling for 2 h and then cooling to room temperature. Then the wet weight (M_3), float weight (M_2) and dry weight (M_1) were recorded. The bulk density (D_b) was calculated using

$$D_b = \frac{M_1 D_1}{M_3 - M_2}, \tag{1}$$

where D_1 is the density of the distilled water. Theoretical density of pure LSCF and GDC was calculated using the lattice parameters obtained from XRD analysis. Theoretical density of LSCF–GDC composites was calculated by the rule of mixture [17]; the simplest mathematical expression for rule of mixture for a binary solid solution A–B is

$$a = a_A(1-x) + a_B x \tag{2}$$

in which a is the property, x is the mole fraction of component B, and $(1-x)$ is the mole fraction of component A.

The sintered bars were about $3 \times 4 \times 50\ mm^3$ in dimension; pellets were about 10 mm in diameter and 2 mm in thickness. Rectangular samples were used for thermal expansion tests and electrical conductivity tests. Thermal expansion properties were measured using a Netzsch 402PC dilatometer in air over a range from the room temperature to 1000 °C with a heating rate 3 °C/min. A standard alumina rod was used for calibration. The average TEC was calculated from the expansion curve using

$$\alpha = \frac{1}{L_0} \frac{\Delta L}{\Delta T} \tag{3}$$

where L_0 is the initial length of the sample, ΔL is the sample length change and ΔT is the range of temperature variation.

Electrical conductivities were measured using the standard DC four probe technique with a Keithley 2440 sourcemeter in a tube furnace in air upon cooling from 800 °C to 200 °C. Two inner platinum wires acted as current contacts and the other outer two wires acted as the voltage contacts. They were attached to the rectangular bars by painting platinum paste along the circumference. A constant current was applied to the current wires and the voltage response on the voltage wires was recorded. The conductivity was determined from a set of I–V values by taking

$$\sigma = \frac{L}{A} \frac{dI}{dV} \tag{4}$$