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Characterization of $Ba_{0.5}Sr_{0.5}M_{1-x}Fe_xO_{3-\delta}$ (M = Co and Cu) perovskite oxide cathode materials for intermediate temperature solid oxide fuel cells

Ki-Woog Song [a], Ki-Tae Lee [a,b,*]

[a] Division of Advanced Materials Engineering, Chonbuk National University, Jeonbuk 560-756, Republic of Korea
[b] Hydrogen and Fuel Cells Research Center, Chonbuk National University, Jeonbuk 560-756, Republic of Korea

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Abstract

$Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_xO_{3-\delta}$ ($x = 0.2$, 0.6, and 0.8) and $Ba_{0.5}Sr_{0.5}Cu_{1-x}Fe_xO_{3-\delta}$ ($x = 0.6$ and 0.8) perovskite oxides have been investigated as cathode materials for intermediate temperature solid oxide fuel cells. All the samples synthesized by a citrate–EDTA complexing method were single-phase cubic perovskite solid solutions. Then, the thermal expansion coefficient, electrical conductivities, the oxygen vacancy concentrations, the polarization resistances (R_p), and the power densities were measured. An increase in the Co content resulted in a decrease in the polarization resistance, the electrical conductivities at low temperatures, and the inflection point of the thermal expansion coefficient, but it led to an increase in the electrical conductivities at high temperatures, the oxygen vacancy concentrations, and the maximum power densities. The Cu-based system has similar behavior to the Co-based system; yet, in terms of the electrical conductivities, high Cu content gave a better result than low content for the entire range of temperatures.

Keywords: C. Electrical conductivity; C. Thermal expansion; D. Perovskite; Solid oxide fuel cells

1. Introduction

Solid oxide fuel cells (SOFCs) have high energy conversion efficiency, low pollution emissions, and other environmental advantages that make them an attractive alternative to other energy conversion devices. Recently, intermediate temperature SOFCs (IT-SOFCs), which operate in the range of 500–800 °C, have drawn attention due to their versatility in terms of components, mechanical stability, decreased chemical reactivity, and other favorable attributes. Unfortunately, conventional cathode materials such as $La_{1-x}Sr_xMnO_3$ do not have enough catalytic activity to induce the oxygen reduction reaction in the intermediate temperature range due to their low oxygen ion vacancy concentrations, which result in low oxygen permeability and thereby limit the oxygen reduction rates in the triple-phase boundary (TPB) [1,2]. Consequently, discovering alternative candidates for IT-SOFC cathodes has become a high research priority.

Mixed-conduction perovskite oxides have been extensively explored as cathode materials for IT-SOFCs because they possess an ideal combination of electronic and ionic conductivities, a beneficial electrochemical reaction, and a fine structural stability [3–8]. In particular, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) has been reported to perform exceptionally well as an IT-SOFC cathode material [9–13].

Since Shao et al. first discovered $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), which substitutes Ba, a divalent alkaline-earth element, for La, a trivalent rare-earth element, in the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ composition, and BSCF and modified-BSCF have been widely studied as promising cathode materials in IT-SOFCs [6–8,14–16]. BSCF is a prospective cathode material because it has a high catalytic activity for the oxygen reduction reaction and a good oxygen diffusion rate [6–8,14]; however, BSCFs with a high Co content also have a large thermal expansion coefficient (TEC), which can cause considerable problems, such as decreased mechanical stability with the other cell components [17–19].

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* Corresponding author at: Division of Advanced Materials Engineering, Chonbuk National University, Jeonbuk 560-756, Republic of Korea.
Tel.: +82 63 270 2290; fax: +82 63 270 2386.
E-mail address: ktlee71@jbnu.ac.kr (K.-T. Lee).

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Thus, the objective of this study was to improve the electrical conductivity and reduce the TEC of BSCF by substituting various amounts of Co and Cu onto the B site of BSCF, all while retaining its remarkable electrochemical reaction. To do so, $Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_xO_{3-\delta}$ ($x = 0.2$, 0.6, and 0.8; BSCoF) and $Ba_{0.5}Sr_{0.5}Cu_{1-x}Fe_xO_{3-\delta}$ ($x = 0.6$ and 0.8; BSCuF) were synthesized using a citrate–EDTA complexing method, and the effects of Co and Cu on the oxide ion vacancy concentrations, the TECs, the electrical conductivities, and the electrochemical performances were investigated. In addition, all the compositions were compared to LSCF to determine their relative performances.

2. Experimental procedure

All cathode powders were synthesized using a citrate-EDTA complexing method [20]. The nomenclature for each composition is listed in Table 1. The required amount of ethylene-diamine-tetraacetic acid (EDTA) was initially dissolved in aqueous NH_4OH. The stoichiometric quantity of metal nitrates, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}2.5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, and $La(NO_3)_3{\cdot}6H_2O$, for each composition was then added to the EDTA–NH_4OH solution under stirring. Next, an appropriate amount of citric acid was mixed with the solution, and NH_4OH was added until the pH reached ~8. The molar ratio of the EDTA/citric acid/metal ions was 1:1.5:1. The precursor was kept at 90 °C with stirring to evaporate the water. After transparent gels were obtained, they were dried in an oven at 130 °C for 24 h, creating porous ashes. These ashes were then calcined at 900 °C for 5 h in air to obtain end-products possessing a single phase of the perovskite structure. The $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) electrolyte was prepared by the urea combustion method [21]. The dense GDC electrolyte was sintered at 1450 °C for 4 h, and the anode powder (Ni:YSZ = 60:40 vol%) was prepared by ball milling for 12 h with NiO (FP, Japan) and 8YSZ (Tosoh, Japan) commercial powders.

The phase identification of the prepared powders was carried out using an X-ray diffractometer (XRD, D/MAX-111A, Rigaku Corporation, Japan) with a scanning speed of 4°/min using Cu Kα radiation. Microstructural characterization of the prepared samples was carried out with a scanning electron microscope (SEM, SN-3000 Hitachi, Japan). Iodometric titration was performed at room temperature in order to investigate the oxygen vacancy concentration, δ, for all the cathode compositions except LSCF. The variation of oxygen contents with temperature (25–900 °C) was assessed with a Perkin-Elmer Series 7 thermogravimetric analyzer (TGA) in air with a heating/cooling rate of 2 °C/min. In order to exclude moisture effect, all samples were heated at 200 °C for 6 h before TGA experiment. The electrical conductivities were measured via a four-probe DC method in the range of 300-800 °C at 50 °C increments in air and oxygen atmosphere, respectively. Thermal expansion coefficients (TECs) were observed using TMA from room temperature to 800 °C with a heating/cooling rate of 2 °C/min in air. For the electrical conductivity and TEC measurements, the BSCoF, BSCuF, and LSCF samples were sintered at 1100, 900, and 1200 °C for 5, 10, and 5 h, respectively. All the samples used for conductivity and TEC measurements had densities greater than 95% of the theoretical values.

Electrochemical performances were evaluated via AC impedance analysis and current–voltage (*I–V*) measurements with electrolyte-supported symmetrical half cells and single cells, respectively. The screen printed cathodes were fired at 925 °C (BSCuF) and 1000 °C (BSCoF and LSCF) for 2 h. The symmetrical half cells with a geometrical electrode area of

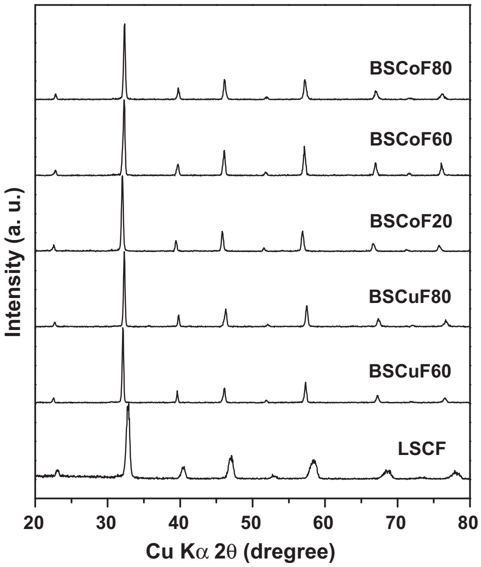

Fig. 1. X-ray diffraction patterns of $Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_xO_{3-\delta}$ ($x = 0.2$, 0.6, and 0.8), $Ba_{0.5}Sr_{0.5}Cu_{1-x}Fe_xO_{3-\delta}$ ($x = 0.6$ and 0.8), and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) oxides calcined at 900 °C for 5 h.

Table 1
Nomenclature for the synthesized powders.

Composition	Abbreviation
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	BSCoF20
$Ba_{0.5}Sr_{0.5}Co_{0.4}Fe_{0.6}O_{3-\delta}$	BSCoF60
$Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$	BSCoF80
$Ba_{0.5}Sr_{0.5}Cu_{0.4}Fe_{0.6}O_{3-\delta}$	BSCuF60
$Ba_{0.5}Sr_{0.5}Cu_{0.2}Fe_{0.8}O_{3-\delta}$	BSCuF80
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	LSCF

Table 2
B-site mean valence and oxygen content ($3 - \delta$) data as measured by iodometric titration at room temperature.

Composition	Mean valence of B-site cations	Oxygen content ($3 - \delta$)
BSCoF20	3.24	2.62
BSCoF60	3.27	2.64
BSCoF80	3.33	2.67
BSCuF60	2.90	2.45
BSCuF80	2.98	2.49
LSCF	3.35 [26]	2.97 [26]