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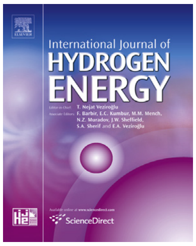

Evaluation of $(Bi_{0.4}Sr_{0.6})_xCo_{0.3}Fe_{0.7}O_{3-\delta}$ ($x = 0.7, 0.8, 0.9, 1.0, 1.1$) perovskite-type oxide as potential cathode for intermediate-temperature solid oxide fuel cells

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ABSTRACT

Perovskite-type $(Bi_{0.4}Sr_{0.6})_xCo_{0.3}Fe_{0.7}O_{3-\delta}$ (BiSCF) oxides with various A-site proportions ($x = 0.7$, 0.8, 0.9, 1.0 and 1.1, denoted as BiSCF407, BiSCF408, BiSCF409, BiSCF410 and BiSCF411, respectively) have been developed and investigated as cathode for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The crystal structure of the BiSCF sample is refined based on the Pm-$3m$ space group with perfectly cubic structure ($a = a_0$). The cells with thick $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\sigma}$ (LSGM) electrolyte (0.5 mm thickness) and symmetrical BiSCF electrodes are fabricated for electrocatalaytic activity test and it is found that the cell with BiSCF408 shows the lowest polarization resistance of 0.10 Ω cm^2 at 700 °C. The LSGM electrolyte-supported (~300 μm thickness) cell with BiSCF408 cathode exhibits power densities of 0.34 and 0.46 W cm^{-2} at 650 and 700 °C, respectively, with humidified H_2 (~3% H_2O) as the fuel and ambient air as the oxidant. Over 100 h stability test at 600 °C indicates that a little performance decrease occurs but no interfacial damage happens even after the long-term operation, suggesting that BiSCF408 is a potential material for IT-SOFCs.

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Introduction

Solid oxide fuel cells (SOFCs) are a type of electrochemical device with high energy conversion effectivity which can convert chemical energy directly into electrical power with flexible fuel choice and minimal environmental impact [1–4]. Unfortunately, the conventional SOFCs have to be operated at high temperatures (800–1000 °C) and could result in components degradation and should resolve some technical obstacles. It is important to reduce cost and improve performance for large-scale application of SOFC. Lowering of the operation temperature down to intermediate range (600–800 °C) is one of ways to overcome the stability problem of the constituent components during long-term operation [5–8]. However, decreasing of the operating temperature could lower the overall efficiency of intermediate-temperature SOFCs (IT-SOFCs) since cathode polarization usually dominates the total cell resistance and lowering the operation temperature generally result in the resistance increase. Thus, the development of new cathode materials with sufficient electrocatalytic activity at reduced temperatures becomes an important issue for IT-SOFCs research.

A good cathode material requires sufficient mixed ionic and electronic conductivity [9–11]. By far the most widely studied oxide for SOFC cathode is perovskite oxide (ABO_3) and typically based on Sr-doped $LaMnO_3$ (LSM) [12–16]. However, LSM exhibits fairly poor electrocatalytic activity in a temperature below 800 °C [17,18]. To improve its performance in the intermediate temperature range, substitution of Mn by Co or Fe on B-sites (LSCF: $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\sigma}$) becomes a general way [19–22]. Furthermore, it is found that when the A-site La is replaced by Ba (BSCF: $Ba_{1-x}Sr_xFe_{1-y}Co_yO_{3-\sigma}$), higher concentration and mobility of oxygen vacancies can be formed, which are beneficial for oxygen–ionic exchange and transport kinetics [23–27]. However, the presence of Ba^{2+} results in the detrimental structural transformation into a hexagonal perovskite [28,29]. To solve this problem, recently, perovskite accommodating Bi^{3+} on the A-site has been proposed as a novel SOFC cathode material [30–34]. Bi^{3+}, which is highly polarizable owing to its 6s lone pair and lower basicity compared to Ba^{2+}, is expected to increase the structural stability and offer a higher mobility of oxygen vacancies. Moreover, the previous works demonstrated that the introducing of A-site nonstoichiometry (A-site deficiency/excess) into the lattice structure of perovskite oxide imposes the significant impact on the physical–chemical properties of such materials, including the increase of the electrocatalytic activity and stability [35–39].

The aim of the present study is to develop new bismuth-based perovskite oxide materials $(Bi_{0.4}Sr_{0.6})_xCo_{0.3}Fe_{0.7}O_{3-\delta}$ (BiSCF), with the major focus on the effect of A-site nonstoicihiometry (not only A-site deficiency, but also A-site excess) on their suitability as cathode materials for IT-SOFCs. Their structure, compatibility with $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\sigma}$ (LSGM) electrolyte, and oxygen reduction reaction (ORR) on it are investigated. Performances of the LSGM electrolyte-supported single cell with the optimum BiSCF cathode composition and Ni–$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) anode are also evaluated. It is expected to find a potential new cathode material for IT-SOFCs.

Experimental

Materials synthesis

$(Bi_{0.4}Sr_{0.6})_xCo_{0.3}Fe_{0.7}O_{3-\delta}$ (BiSCF) with initial $x = 0.7$, 0.8, 0.9, 1.0 and 1.1, designated as BiSCF407, BiSCF408, BiSCF409, BiSCF410 and BiSCF411, respectively, were synthesized through solid state reaction from the high-purity starting materials of $Bi(NO_3)_3.5H_2O$, $Sr(NO_3)_2$, $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_3.9H_2O$, and $Ce(NO_3)_3.6H_2O$ (Wako, Japan 99.9%). Stoichiometric amounts of these powders were mixed and ball milled at a rotation speed of 300 rpm for 6 h in ethanol media. The resulting precursor solutions were evaporated at 80 °C for 24 h and thoroughly ground in an agate mortar and calcined at different temperatures from 900 to 1000 °C for 8 h in air to obtain the BiSCF powders. GDC ($Ce_{0.9}Gd_{0.1}O_{1.95}$) powder as a composite anode material was also prepared by the solid state reaction from the appropriate proportions of Ce and Gd nitrates (Wako, Japan 99.9%) mixed with ethanol by ball milling. Then the mixture was evaporated and calcined at 900 °C for 5 h in air to gain the GDC powder. The commercial NiO (Soekawa Chemicals, Japan) and $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\sigma}$ (LSGM, FCM, USA) powders were used as received without further purification for the preparation of anode and electrolyte, respectively.

Microstructural and morphological characterizations

X-ray diffraction patterns (XRD, Rigaku SmartLab X-Ray Diffractometer) using Cu-Kα ($\lambda = 1.5405$ Å) radiation source over the angular range of $20° \leq 2\theta \leq 80°$ and a scan rate of 5°/min were employed to examine the phase composition and lattice structure of the sample. Structural refinement was fitted using the POWDERX and PDXL2 Rigaku Data Analysis Software package. The chemical compatibility between BiSCF cathode and LSGM electrolyte was evaluated by XRD analysis after thoroughly mixed with a weight ratio of 1:1 and calcined at 950 °C for 5 h in air. The microstructure of electrode and elemental distribution across cathode-electrolyte interface were investigated by a scanning electron microscope (SEM, Hitachi SU8010) equipped with a Horiba Scientific energy dispersive spectrometer (EDS) analyzer, respectively. EDS data was analyzed using Horiba Emax Version 2.1 software.

Fabrication and testing of cells

LSGM electrolyte supported cell were fabricated to evaluate the electrochemical performance and stability of the BiSCF cathode. LSGM powder was uniaxially pressed at 250 MPa and sintered at 1450 °C for 10 h to obtain dense LSGM electrolyte pellets with 20 mm in diameter.

To investigate the electrochemical behaviour, BiSCF|LSGM|BiSCF symmetrical cells were prepared. The as-synthesized powders were mixed with 80 wt.% organic additives (α-terpineol + ethyl cellulose) solution to produce the cathode slurry. The slurry was then screen-printed on both sides of the LSGM pellet (thickness of 0.5 mm) using the screen printing technique, dried and subsequently sintered at 950 °C for 1 h in air to form a symmetrical cell.