



Enhancement of electrochemical performance and thermal compatibility of $\text{GdBaCo}_{2/3}\text{Fe}_{2/3}\text{Cu}_{2/3}\text{O}_{5+\delta}$ cathode on $\text{Ce}_{1.9}\text{Gd}_{0.1}\text{O}_{1.95}$ electrolyte for IT-SOFCs

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ABSTRACT

Transition-metal doped double-perovskite structure oxides $\text{GdBaCo}_{2/3}\text{Fe}_{2/3}\text{Ni}_{2/3}\text{O}_{5+\delta}$ (FN-GBCO), $\text{GdBaCo}_{2/3}\text{Fe}_{2/3}\text{Cu}_{2/3}\text{O}_{5+\delta}$ (FC-GBCO), $\text{GdBaCoCuO}_{5+\delta}$ (C-GBCO) and pristine $\text{GdBaCo}_2\text{O}_{5+\delta}$ (GBCO) were synthesized via a citrate combustion method. The thermal-expansion coefficient (TEC) and electrochemical performance of the oxides were investigated as potential cathodes for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The TEC exhibited by the FC-GBCO cathode up to 900 °C is $14.6 \times 10^{-6} \text{ °C}^{-1}$, which is lower than the value of GBCO ($19.9 \times 10^{-6} \text{ °C}^{-1}$). Area specific resistances (ASR) of $0.165 \text{ } \Omega \text{ cm}^2$ at 700 °C and $0.048 \text{ } \Omega \text{ cm}^2$ at 750 °C were achieved for the FC-GBCO cathode on a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) electrolyte. An electrolyte supported (300 μm thick) single-cell configuration of FC-GBCO/CGO/Ni-CGO attained a maximum power density of 435 mW cm^{-2} at 700 °C. The unique composition of GBCO co-doped with Fe and Cu ions in the Co sites exhibited reduced TEC and enhancement of electrochemical performance and good chemical compatibility with CGO, and this composition is proving to be a potential cathode for IT-SOFCs.

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1. Introduction

Intermediate-temperature solid oxide fuel cells (IT-SOFCs) with high working efficiency at 500–750 °C have gained considerable importance in the area of power fabrication [1–4]. Recently, simple perovskite-type mixed ionic-electronic conducting (MIEC) oxides, such as doped BaCoO_3 , LaCoO_3 and LaFeO_3 have attracted attention as candidate cathode materials. In MIEC oxides, the penetration of conducting oxygen-ions into the electrode bulk greatly increases the active sites for oxygen-reduction, which lowers interfacial polarization [5]. More recent studies on new types of MIEC oxides, i.e. cation ordered $\text{LnBaCo}_2\text{O}_{5+\delta}$ (Ln = Gd, Pr, Y and La) with two dimensional ion-diffusion channels have shown them to be attractive potential cathode materials for IT-SOFCs. In particular, $\text{GdBaCo}_2\text{O}_{5+\delta}$ (GBCO) has been reported to exhibit ionic conductivity due to the oxygen vacancies that are mainly located in the rare-earth planes $[\text{GdO}]_x$ and high electronic conductivity due to the metal-insulator transition (at 87 °C) [6–8].

The GBCO exhibits a high thermal-expansion coefficient (TEC) $20.1 \times 10^{-6} \text{ °C}^{-1}$ [9], as commonly observed in cobalt-based oxides, which is undesirable for practical use as a cathode for SOFCs [10]. Hence, a systematic investigation on the optimization of TEC and electrochemical performance is essential for the double-

perovskite oxides to be used as potential cathodes in IT-SOFCs. In the present study, oxides of Fe, Ni and Cu doped $\text{GdBaCo}_2\text{O}_{5+\delta}$ were synthesized via a citrate combustion method. The thermal and chemical compatibilities of the cathodes with $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) and the area specific resistance (ASR) by electrochemical impedance spectroscopy were studied. A single-cell electrochemical performance of the FC-GBCO cathode on the CGO electrolyte support and Ni-CGO as the anode was also investigated.

2. Experiment

Double-perovskite oxides of $\text{GdBaCo}_{2/3}\text{Fe}_{2/3}\text{Ni}_{2/3}\text{O}_{5+\delta}$ (FN-GBCO), $\text{GdBaCo}_{2/3}\text{Fe}_{2/3}\text{Cu}_{2/3}\text{O}_{5+\delta}$ (FC-GBCO), $\text{GdBaCoCuO}_{5+\delta}$ (C-GBCO) and pristine $\text{GdBaCo}_2\text{O}_{5+\delta}$ (GBCO) were synthesized via the citrate combustion method. Analytical grade $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (>99.9%), $\text{Ba}(\text{NO}_3)_2$ (99 + %), $\text{Co}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (98 + %), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as precursors for the synthesis of oxide powders, and citric acid (99%) was used as fuel for the combustion reaction.

Initially, stoichiometric amounts of the precursors were dissolved in deionized water with constant stirring, and then citric acid was added to the clear solution. The resultant transparent solution was heated at 70 °C until sufficient water had evaporated, and a transparent gel was obtained. The gel was heated at 125 °C in an oven for 24 h. The dried gel was pre-fired at 250 °C and subsequently calcined at 400 °C for 10 h and 900 °C for 20 h to yield the desired crystalline oxide powders.

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The phase of synthesized powders was characterized with an X-ray diffractometer (XRD) (Rigaku, D/MAX-IIIC X-ray diffractometer) equipped with Cu-K α radiation ($\lambda = 0.15406$ nm). The TEC for each rectangular-shape pellet sintered at 1000–1100 °C for 2 h was measured using a dilatometer (NETZSCH DIL402C) from 30 to 900 °C. The cross-sectional microstructures of the cathode coated on the CGO pellets were characterized by a scanning electron microscope (FE-SEM Philips XL30 FEG).

The symmetrical half-cells were fabricated by screen-printing the cathode inks, prepared by mixing the cathode powders with ethyl cellulose, α -terpineol, and dibutylphtalate, on either side of the dense sintered CGO pellets to form a working electrode (WE) and a counter electrode (CE). The as-fabricated half-cells were sintered at 950 °C for 2 h in air to form an effective cathode surface area of 0.385 cm² and a thickness of ~ 15 μ m. Pt paste (ESL) was applied to the edge of the same side of the WE on the electrolyte to act as a reference electrode (RE). The ASR measurement was carried out using impedance spectroscopy (Solartron 1260 impedance/Gain-phase analyzer) in the frequency range of 10⁶–10⁻² Hz with a voltage amplitude of 10 mV as a function of temperature (600–800 °C) in flowing air.

A single-cell was fabricated by initially screen-printing NiO–CGO (in a weight ratio of 65:35) as the anode on one side of the dense CGO electrolyte pellet (300 μ m thick) and was sintered at 1300 °C for 2 h followed by FC-GBCO cathode coating on the opposite side. The single-cell was then sintered at 950 °C for 2 h. The single-cell was sealed at one end of an alumina tube using ceramic adhesive. A Keithley 2400 Sourcemeater was used to measure I – V polarization under flowing humidified H₂ ($\sim 3\%$ H₂O) as fuel and air as oxidant.

3. Result and discussions

Fig. 1a shows the XRD patterns of the doped GBCO powders calcined at 900 °C for 20 h. The XRD patterns of pristine and doped GBCO oxides exhibit phase pure, high crystalline double-perovskite structure with no peaks attributable to impurities detected [11–13]. All the diffraction peaks of GBCO and FN-GBCO can be indexed based on the JCPDS #53–0135 with an orthorhombic symmetry, space group $Pmmm$. On the other hand, FC-GBCO and C-GBCO exhibited tetragonal symmetry, space group $P4/mmm$ [11,13]. The unit cell parameters for tetragonal symmetry FC-GBCO are $a = 3.885$ Å, $b = 3.884$ Å and $c = 7.635$ Å, and the cell volume is 115.255 Å³. Tarancón et al. [13] described the high-temperature phase transition of GdBaCo₂O_{5+ δ} as occurring at ca. 475–500 °C and corresponding to a symmetry change from orthorhombic $Pmmm$ to the tetragonal $P4/mmm$ phase. Taskin et al. [12] observed that for values of oxygen concentration below $\delta < 0.45$, GdBaCo₂O_{5+ δ} shows tetragonal symmetry while above it ($0.45 < \delta < 0.60$) becomes orthorhombic (at room temperature). In the present study, the Cu or Fe and Cu doped GBCO retained the tetragonal symmetry at room temperature, which involves oxygen stoichiometry below $\delta < 0.45$.

Fig. 1b shows the thermal-expansion curves for doped GBCO cathodes measured from 30 to 900 °C. The inset Table in Fig. 1b shows the average TEC values of the doped GBCO cathodes for different temperature ranges, 100–350, 600–900 and 30–900 °C, and compares the calculated TEC values with the reported TEC values of GBCO by Li et al. and Tarancón et al. [9,13]. The observed reduced TEC for doped GBCO cathodes compared with GBCO would be due to the substitution of Co by Fe, Ni and Cu cations that contribute to a reduced effect of both the spin-state transitions of Co³⁺ and the formation of oxide ion vacancies. Similar trends with the replacement of Co ions by other transition metal ions leads to a decrease in TEC have been observed with various cobalt-based sys-

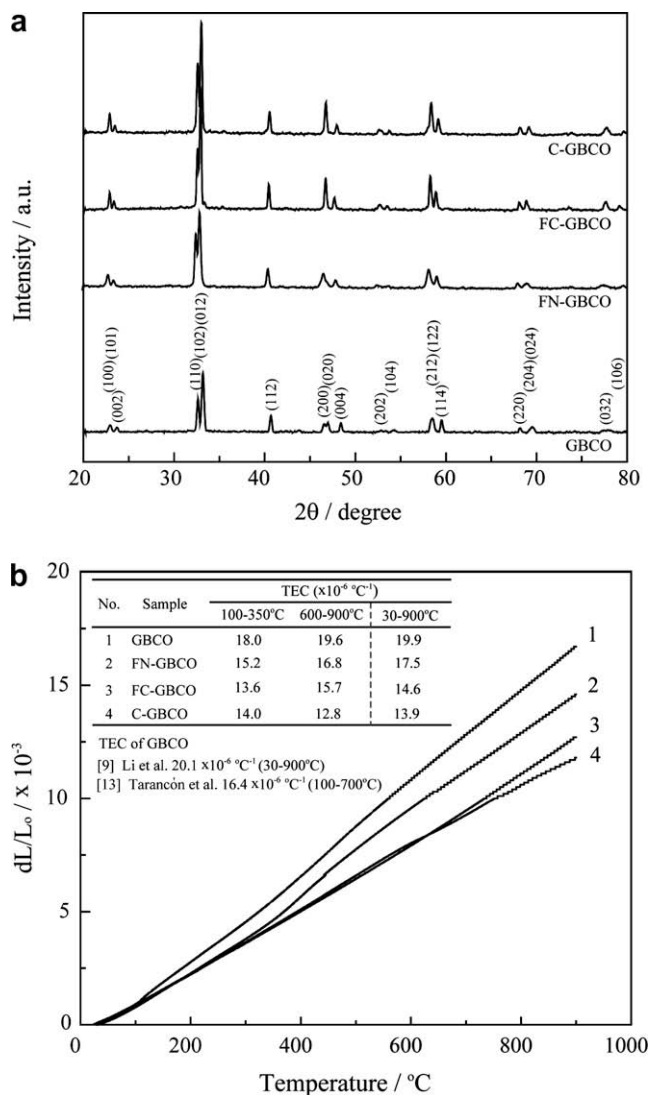


Fig. 1. (a) XRD patterns of doped GBCO powders calcined at 900 °C for 20 h and (b) Thermal-expansion (dL/L_0) curves of doped GBCO in the temperature range of 30–900 °C in air. Inset Table shows the TEC values for doped GBCO.

tems, including Nd_{0.6}Sr_{0.4}Co_{0.8}M_{0.2}O_{3- δ} (M = Ti, Cr, Mn, Fe, Co and Cu) [14] and La_{1-x}Sr_xCo_{1-y}Fe_yO_{3- δ} [15] in the previous reports. The larger TEC values with the cobalt-based perovskite oxides can be attributed to the electronic spin-state transition associated with low-spin-state ($t_{2g}^6 e_g^0$) to high-spin-state ($t_{2g}^5 e_g^2$) of Co³⁺ ions, and the high spin-state ion is larger in size compared to the low-spin-state ion [16]. Alternatively, the formation of oxide ion vacancies results in a reduction of the transition metal ions and a consequent increase in the ionic size and a decrease in the overall lattice binding energy [13,17,18]. Thus, in the present study, the substitution of Fe, Ni and Cu cations for Co ions is advantageous to achieve the reduced TECs of the doped GBCO oxides.

The calculated ASR values from the interface resistances of the impedance spectra are shown in Fig. 2. An inset in Fig. 2 shows a typical impedance spectrum for the symmetrical cells fabricated with the FC-GBCO oxide on the CGO electrolyte, measured at 650, 700 and 750 °C. The intercepts of the semicircle on the real axis at high-frequency region represent the total ohmic resistance of the electrolyte and current collector wires. The resistance between the two intercepts of the semicircle at low-frequency and the high-frequency regions on the real axis corresponds to the polarization resistance of the cathodes. In Fig. 2, the Fe and Cu

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