Short communication

Improved electrochemical performance and thermal compatibility of Fe- and Cu-doped $SmBaCo_2O_{5+\delta}$–$Ce_{0.9}Gd_{0.1}O_{1.95}$ composite cathode for intermediate-temperature solid oxide fuel cells

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ABSTRACT

Fe- and Cu-doped $SmBaCo_2O_{5+\delta}$ (FC-SBCO)–$Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) composites with various CGO contents (0–40 wt.%) are investigated as new cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFCs) based on a $Ce_{0.9}Gd_{0.1}O_{1.95}$ electrolyte. The effect of CGO incorporation on the thermal expansion coefficient (TEC), electrochemical properties and thermal stability of the FC-SBCO-CGO composites is investigated. A composite cathode of 30 wt.% CGO–70 wt.% FC-SBCO (CS30-70) coated on a $Ce_{0.9}Gd_{0.1}O_{1.95}$ electrolyte shows the lowest area specific resistance (ASR), i.e., $0.049\,\Omega\,cm^2$ at 700 °C. The TEC of the CS30-70 cathode is $14.1 \times 10^{-6}\,°C^{-1}$ up to 900 °C, which is a lower value than that of the FC-SBCO ($16.6 \times 10^{-6}\,°C^{-1}$) counterpart. Long-term thermal stability and thermal cycle tests of the CS30-70 cathode are performed. Stable ARS values are observed during both type of test. An electrolyte-supported (300-μm thick) single-cell configuration of CS30-70/CGO/Ni-CGO delivers a maximum power density of $535\,mW\,cm^{-2}$ at 700 °C. The unique composite composition of CS30-70 demonstrates improved electrochemical performance and good thermal stability for IT-SOFCs.

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1. Introduction

Solid oxide fuel cells (SOFCs) are considered promising power generation devices because of their high working efficiency, low pollution, and fuel flexibility [1–4]. In the intermediate-temperature region (600–800 °C), the cathode becomes the limiting factor in determining the overall cell performance because the polarization resistance increases rapidly as the temperature decreases [2,5]. Thus, the development of new electrodes with high electrocatalytic activity for the oxygen-reduction reaction is significant for IT-SOFCs. Much effort has been devoted to the development of mixed ionic and electronic conductors (MIECs), such as Sr- and Fe-doped $BaCoO_3$ (BSCF) and $LaCoO_3$ (LSCF), that show excellent catalytic activity.

Recently, several research groups have reported the electrochemical properties of a new type of MIEC oxide, cation ordered $LnBaCo_2O_{5+\delta}$ (Ln = La, Pr, Sm, Gd, Y), as a potential cathode material for IT-SOFCs [2,6–8]. Cobalt in cathodes is beneficial for the activation of oxygen reduction and thus provides a lower activation polarization loss [3,4]. Cobalt-based cathodes, however, have high thermal expansion coefficients (TECS) because of the low-spin to high-spin transition of Co [4,5,8]. The incompatibility in thermal expansion can cause thermal stress in SOFCs and thus result

in poor long-term thermal stability [5,9]. Therefore, it is important to improve the thermal expansion compatibility between the cathodes and the electrolytes. More recently, the authors' group reported that Co site doped $GdBaCo_2O_{5+\delta}$ (GBCO) exhibits a lower TEC and an enhancement of electrochemical performance [8]. Kim and Manthiram have reported the effect of the Ln ion radius on the TEC and electrochemical performance [6]. They demonstrated a decrease in Ln^{3+} ion radii, leading to a decrease in power density and TEC. Encouraged by these previous reports, a Fe- and Cu-doped $SmBaCo_2O_{5+\delta}$ cathode has been developed because it may provide a compromise between TEC and power density.

Recently, composite cathodes have been of great interest because they can expand the electrochemically-active triple-phase boundaries, enhance electrochemical performance and reduce the TEC [2,3]. With the aim of improving electrochemical performance and reducing the mismatch in TEC between the electrolyte and cathode materials, an evalutation is made of the electrochemical performance and thermal stability of Fe- and Cu-doped $SmBaCo_2O_{5+\delta}$ (SBCO) and CGO composite cathodes.

2. Experimental

A double-perovskite oxide of $SmBaCo_{2/3}Fe_{2/3}Cu_{2/3}O_{5+\delta}$ (FC-SBCO) was synthesized via a citrate combustion method, and composite cathodes were synthesized via a precipitation method. Detailed synthesis methods of FC-SBCO and composite cathodes for this have been published elsewhere are available in our previous

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Table 1
Chemical compositions and their designations.

Chemical composition	Designation
$SmBaCo_{2/3}Fe_{2/3}Cu_{2/3}O_{5+\delta}$	FC-SBCO (CSO-100)
$Ce_{0.9}Gd_{0.1}O_{1.95}$	CGO
10 wt.% CGO and 90 wt.% FC-SBCO	CS10-90
20 wt.% CGO and 80 wt.% FC-SBCO	CS20-80
30 wt.% CGO and 70 wt.% FC-SBCO	CS30-70
40 wt.% CGO and 60 wt.% FC-SBCO	CS40-60

works [3,8]. The FC-SBCO and CGO composites had a composition varying from 0 to 40 wt.%; the designations of these cathodes are summarized in Table 1.

The phases of the synthesized powders were characterized with a third-generation synchrotron powder X-ray diffractometer (XRD) from the 8C2 station beam line with Cu Kα radiation (λ = 1.549 Å) at the Pohang Light Source (PLS) in Korea. The TEC for each rectangular-shape pellet sintered at 1000 °C for 2 h was measured using a dilatometer (NETZSCH DIL402C) from 30 to 900 °C at a heating rate of 5 °C min^{-1}. The cross-sectional microstructures of the cells were inspected with a scanning electron microscope (FE-SEM Philips XL30 FEG).

The symmetrical half-cells were fabricated by screen-printing [8]. The as-fabricated half-cells were sintered at 950 °C for 2 h in air. Each electrode had a circular shape with a diameter of 0.7 cm, and its active electrode area was 0.385 cm^2 with a thickness of ~15 μm. The area specific resistances (ASRs) were measured via 3-probe a.c. impedance spectroscopy (Solartron 1260 impedance/Gain-phase analyzer) as a function of temperature (500–800 °C) in flowing air. The sweeping frequency range was 10^6 to 10^{-2} Hz with a signal amplitude of 10 mV. The symmetrical half-cell was thermally cycled between 200 and 650 °C with heating and cooling rates of 5 °C per min. Each ASR was measured after equilibrating for 30 min at a 650 °C. Fifty thermal cycles were performed in sequence. In addition, the long-term thermal stability of the symmetrical half-cell was determined at 650 °C for 500 h.

Electrolyte-supported single-cells with 300 μm of CGO as the electrolyte, CS0-100 and CS30-70 as the cathode, and NiO-CGO (in a weight ratio of 65:35) as the anode were fabricated using a screen-printing method. A source meter (Keithley 2400) was used to measure the I–V polarization under flowing humidified H$_2$ (~3% H$_2$O) as a fuel and in air as an oxidant, respectively, at a rate of 100 sccm.

3. Results and discussion

The synchrotron source XRD patterns of the FC-SBCO and CS30-70 cathodes calcined at 900 °C for 10 h are presented in Fig. 1. The XRD pattern of FC-SBCO is evidence of a single-phase, high crystalline double-perovskite structure without any impurity phase; the indexed primary peaks of FC-SBCO are summarized in Fig. 1. Based on previous reports, [6,7] the structure of $SmBaCo_2O_{5+\delta}$ is orthorhombic in nature and can be changed by the oxygen content or the size of the lanthanide [6,10]. In the present study, the Fe- and Cu-doped SBCO retained the tetragonal symmetry at room temperature, which involves oxygen stoichiometry below δ < 0.45 [8,11]. The unit-cell parameters for FC-SBCO were a = 3.883 Å, b = 3.883 Å and c = 7.627 Å, and the cell volume was 114.998 Å^3. The patterns of the CS30-70 composite show the presence of indexed peaks corresponding to CGO and FC-SBCO without any other secondary phases. The synchrotron XRD investigations confirm that FC-SBCO and CGO have good chemical compatibility.

Fig. 2 shows the thermal expansion curves for composite cathodes with different wt.% CS. The table in the inset shows TEC values calculated from the plots and exhibit the relatively reduced TEC of FC-SBCO (16.6 × 10^{-6} °C^{-1}) compared with pristine SBCO
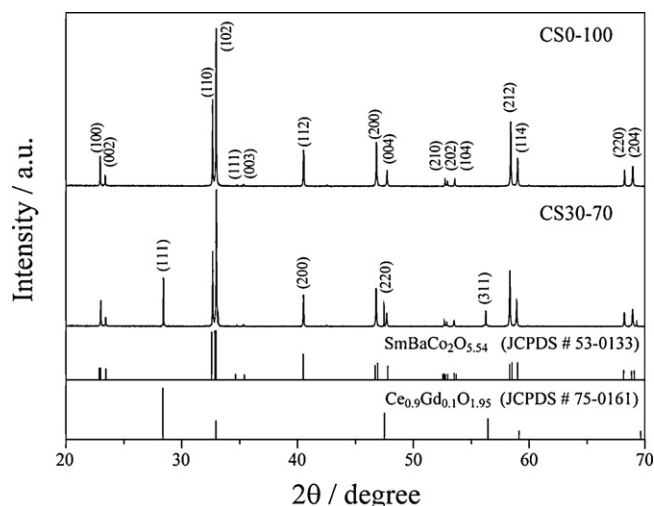

Fig. 1. Synchrotron XRD patterns of $SmBaCo_{2/3}Fe_{2/3}Cu_{2/3}O_{5+\delta}$ (CS0-100) and CS30-70 powers calcined at 900 °C for 10 h and compared the JCPDS data for CGO and $SmBaCo_2O_{5.54}$.

($19\sim20 \times 10^{-6}$ °C^{-1}) [13,14]. Thus, substitution of Fe and Cu in the Co sites of SBCO can control the large thermal expansion characteristic of SBCO. The reduced TEC for Fe- and Cu co-doped SBCO can be explained based on the formation of oxygen vacancies in cobalt systems as reported for LSCF and GBCO [8,15]. The TEC of FC-SBCO, however, is still higher than that of the CGO electrolyte, for example, the TEC of CGO electrolyte is 10.1 × 10^{-6} °C^{-1} in the temperature range of 20–800 °C in air [16].

As expected, a further decrease in the TEC values is observed on the addition of CGO into FC-SBCO. The TEC of CS0-100 decreases to 14.1 × 10^{-6} °C^{-1} for the CS30-70 cathode. The reduction of the TEC of composite cathode is attributed mainly to the smaller TEC of CGO. Thus, the addition of CGO leads to a decrease in the thermal expansion coefficient, which caused the thermal stability of the CS30-70 cathode, as reported below.

The ASR values of the different wt.% CS composites that are calculated from the interface resistances of the impedance spectra are shown in Fig. 3. The two insets (a) and (b) in Fig. 3 show the plot of ASR values vs. different wt.% CS composites and the impedance spectra for the symmetrical half-cells fabricated with pristine and different wt.% CS composites, respectively. The resis-
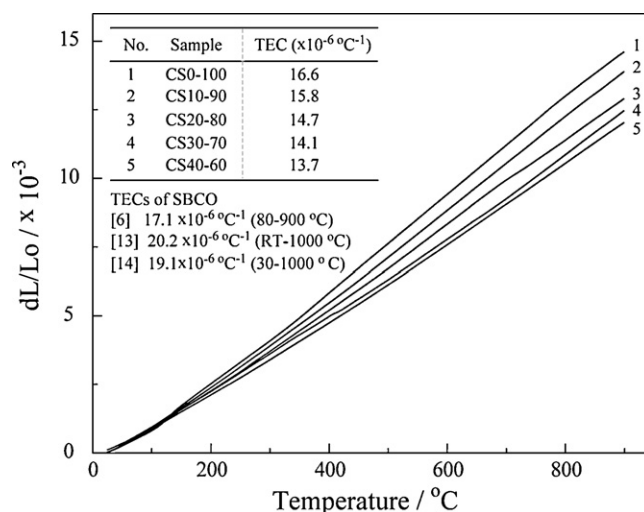

Fig. 2. Thermal-expansion curves (dL/L_0) of CS composites in temperature range of 30–900 °C in air. Inset table shows TEC values for CS composites.
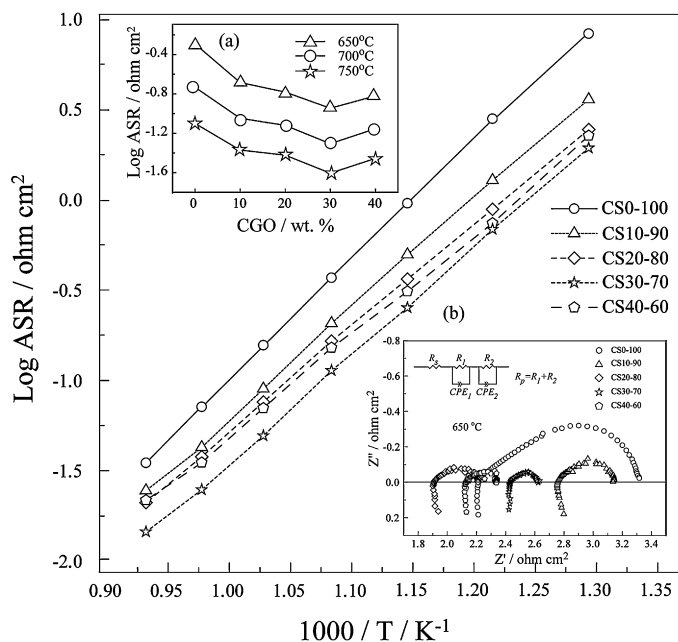
Fig. 3. Arrhenius plots of log ASR for symmetrical cells of different wt.% CS/CGO at interface, measured in air. Inset (a) shows ASR values *vs.* wt.% CS composites. Inset (b) shows impedance spectra of different wt.% CS composites at 650 °C.

tivity ($R_p = R_1 + R_2$) was obtained by fitting the impedance spectrum with an equivalent circuit model (inset (b) in Fig. 3). The intercepts of the semicircle on the real axis at high-frequency region represent the total ohmic resistivity (R_s) of the electrolyte, the current collectors and the lead wires. The resistivity between the two intercepts of the semicircle at high- and low-frequency regions on the real axis corresponds to the polarization resistivity (R_p) of the cathodes [2,4]. It is clear that the ASR decreases as the CGO content increases up to 30 wt.%. The CS30-70 composite cathode on the $Ce_{0.9}Gd_{0.1}O_{1.95}$
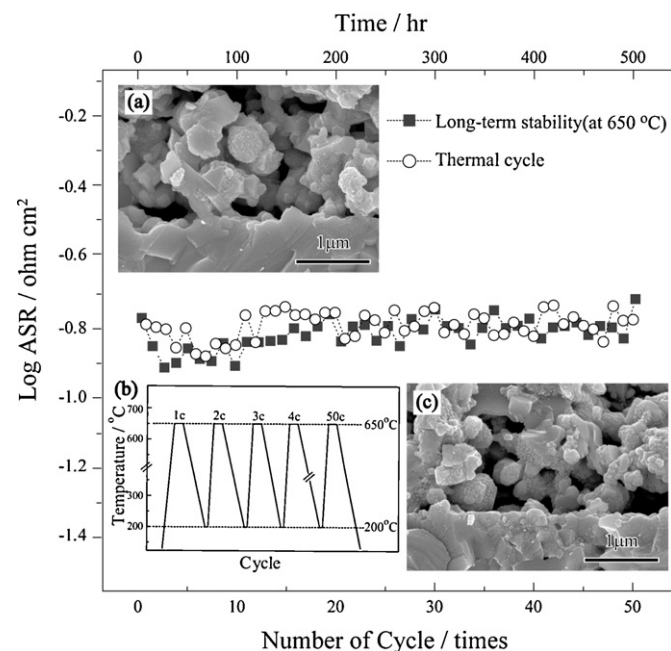

Fig. 4. ASR values of CS30-70 at 650 °C for long-term thermal stability and thermal cycle results under flowing air. Insets (a) and (c) are SEM images of cross-sectional views of interface between cathode and electrolyte after long-term thermal stability and cycle tests, respectively. Inset (b) shows the temperature patterns for thermal cycle test.
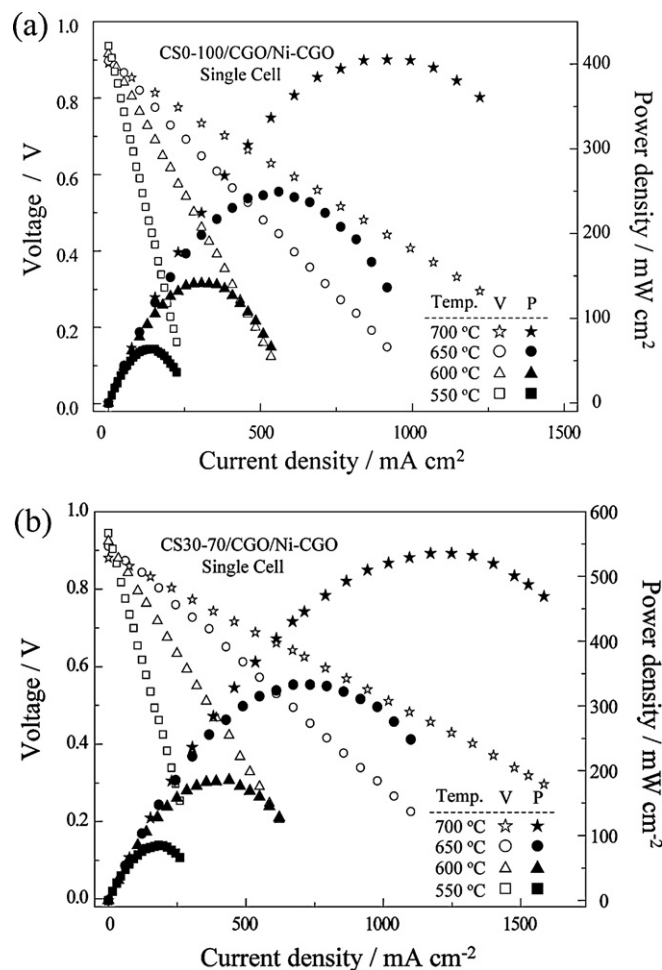

Fig. 5. Electrochemical performance of (a) CS0-100/CGO/Ni-CGO and (b) CS30-70/CGO/Ni-CGO single-cells under humidified H_2 fuel and air oxidant at different temperatures.

(CGO) electrolyte shows an ASR value of $0.049 \Omega \, cm^2$ at 700 °C (see Fig. 3), which is lower than the value for the CS0-100 cathode ($0.184 \Omega \, cm^2$ at 700 °C). The inset (a) clearly reveals that the CS30-70 composite possesses the lowest ASR values at various temperatures. A further increase in CGO content to a value higher than 30 wt.% results in a higher interfacial polarization resistance, which may be due to a decrease in the electron-conducting path that, in term, results in a decrease in the electrical conductivity [2].

It is widely accepted that the addition of a highly conductive phase to the electrode, i.e., composite cathodes, is effective in expanding the electrochemically reaction zone from the limits of the two-dimensional interface between the electrolyte and the cathode to the entire area of cathode, and thereby significantly improves the cathode performance [1–3,12]. As a result, the addition of the high ionic conductive CGO in CS composite cathodes may extend the triple-phase boundaries, and results in much lower overpotentials toward oxygen reduction by providing short-circuit paths for ion transport. These effects reflect a decrease in cathode polarization due to a reduction in charge-transfer resistance [2,3].

To evaluate the thermal stability of the CS30-70 cathode, the ASRs of the half-cell as a function of thermal cycling and long-term thermal stability were surveyed by a.c. impedance spectroscopy; the results are shown in Fig. 4. The half-cell was thermally cycled 50 times between 200 and 650 °C with heating and cooling rates of 5 °C per min, as shown in inset (b) of Fig. 4. The results demonstrate small or negligible changes in polarization resistance after

50 thermal cycles. The CS30-70 cathode also displays stable performance for 500 h at 650 °C in light of changes in the ASR value. Insets (a) and (c) are cross-sectional views of the interface between the CS30-70 cathode and the CGO electrolyte after the cell tests. The SEM micrographs reveal high porosity and good connectivity without cracking or delamination, which lead to the stable polarization resistance during the cell test. The reduced TECs may be one of the reasons behind the stable bonding between the cathode and electrolyte after cycling and long-term thermal stability testing.

The electrochemical performances of the electrolyte-supported single-cell configuration of CS/CGO/Ni-CGO are shown in Fig. 5 for the temperature range of 550–700 °C using humidified H_2 (~3% H_2O) as a fuel and air as an oxidant. The maximum power density of CS0-100 was 405 mW cm^{-2}, and that of CS30-70 was 535 mW cm^{-2} at 700 °C. These results demonstrate that the CS30-70 cathode exhibits high performance in the intermediate-temperature regime, which is compatible with reported data for double-perovskite cathode materials [6,7,17]. Thus, it can be concluded that the enhanced electrochemical performance and structural stability of the CS30-70 cathode is due to the addition of the CGO to the FC-SBCO, which yielded a large triple-phase boundary and provides short routes for ion transport for mixed conducting materials, that are advantageous for efficient oxygen reduction processes and fast charge transport [2,3]. The addition of CGO also affects good interconnectivity between the composite particles and the interface of the cathode and electrolyte due to a reduced TEC. In addition, the performance of the cell may be improved significantly by introducing an anode-supported structure to minimize ohmic polarization, which is mainly attributed to the electrolyte.

4. Conclusions

The different weight percentages of CS0-100 to CS40-60 composite cathodes have been synthesized via a citrate combustion method followed by a precipitation method. The TEC values are reduced by mixing CGO and FC-SBCO particles to form CS composite cathodes, which significantly improves the thermal stability of the CS30-70 cathode by achieving a match of the TEC between the electrolyte and cathode. Among the CS composite cathodes, the CS30-70 cathode gives the highest performance. The maximum power density of the electrolyte-supported single-cell CS30-70/CGO/Ni-CGO is 332 and 535 mW cm^{-2} at 650 and 700 °C, respectively. These results suggest that CS30-70 is a promising cathode material for use in IT-SOFCS.

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