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Evaluation of $GdBaCuCo_{0.5}Fe_{0.5}O_{5+\delta}$ as cathode material for intermediate temperature solid oxide fuel cells

Qingjun Zhou [a,*], Tong Wei [a], Songqing Guo [a], Xuelian Qi [a], Ruifei Ruan [b], Yan Li [a], Yao Wu [a], Qian Liu [a]

[a] *College of Science, Civil Aviation University of China, Tianjin 300300, PR China*
[b] *Engineering Techniques Training Center, Civil Aviation University of China, Tianjin 300300, PR China*

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Abstract

The $GdBaCuCo_{0.5}Fe_{0.5}O_{5+\delta}$ (GBCCF) layered perovskite oxide was evaluated as novel cathode for intermediate temperature solid oxide fuel cells (IT-SOFCs). Its electrical conductivity was 9–13 S cm^{-1} at 650–800 °C in air. The average thermal expansion coefficient (TEC) of GBCCF was 14.4×10^{-6} K^{-1}, which was close to that of the typical electrolyte material. The cathode polarization resistance of GBCCF was 0.650 Ω cm^2 at 750 °C and it decreases to 0.118 Ω cm^2 when $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) was added to form a GBCCF–GDC composite cathode. Preliminary results indicated that layered perovskite GBCCF was a promising alternative cathode material for IT-SOFCs.

Keywords: B. Composites; C. Impedance; D. Perovskites; E. Fuel cells

1. Introduction

In recent years, solid oxide fuel cells (SOFCs) have attracted remarkable attention due to their high energy conversion efficiency, low impact on the environment and excellent fuel flexibility [1,2]. However, SOFCs are not yet economically competitive due to the problems associated mainly with high temperature (800–1000 °C) operation, including long-term stability of the cell components, materials and manufacturing cost, etc. [1]. Therefore, the focus of recent research is aimed at decreasing operation temperature of SOFCs down to intermediate temperature range (600–800 °C) or less [3,4]. One major problem encountered for SOFCs operating at such low temperature is to reduce electrodes polarization losses, especially for the polarization resistance of cathode [5]. Therefore optimization of cathode performance is becoming essential for intermediate temperature solid oxide fuel cells (IT-SOFCs).

Recently, $LnBaCuMO_{5+\delta}$ (Ln = rare-earth elements) perovskites have received considerable interest as one of the most promising cathode materials for solid oxide fuel cells, because this oxide material has desirable characteristics including small mismatch in thermal expansion coefficient (TEC) with electrolyte, and high catalytic activity [6–15]. The properties of $GdBaCuCoO_{5+\delta}$ (GBCC) oxides using as cathode materials for IT-SOFCs have been investigated in our precious work [11]. It has been shown that the oxide GBCC is very promising candidate as cathode material for application in IT-SOFCs. However, cobalt-based cathodes often encountered some problems like high TEC, poor stability and high cost of cobalt element, which is undesirable for practical use as a cathode for SOFCs. Hence, in order to optimization of cobalt-based cathodes, partial substitution of cobalt element with other elements in these materials could potentially mitigate these disadvantages while keeping adequate electrochemical activity of cobalt-containing cathode materials.

In this work, oxide of Fe doped $GdBaCuCoO_{5+\delta}$ was synthesized via a solid-state reaction method. $GdBaCuCo_{0.5}Fe_{0.5}O_{5+\delta}$ (GBCCF) was evaluated as an alternative cathode material for IT-SOFCs in terms of TEC match with the

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* Corresponding author. Fax: +86 022 24092514.
E-mail address: zhouqingjun2004@yahoo.com.cn (Q. Zhou).

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electrolytes, electrical conductivity, and electrochemical activity towards the oxygen reduction properties.

2. Experimental

The $GdBaCuCo_{0.5}Fe_{0.5}O_{5+\delta}$ (GBCCF) powders were synthesized using a solid-state reaction. Stoichiometric amounts of commercial powders Gd_2O_3 (99.99%), $BaCO_3$ (99%), CuO (99%), Co_3O_4 (99%), Fe_2O_3 (99.5%) were ground thoroughly with ethanol as grinding medium using an agate pestle and mortar. The obtained precursors were then pressed into pellets and calcined repeatedly at 950, 970 and 1000 °C for 10 h in air with intermediate grindings, respectively. Powders of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) electrolyte were synthesized by glycine-nitrate process (GNP) [16].

In order to improve the electrochemical properties of GBCCF cathode, GBCCF–GDC were prepared by adding different amounts of GDC powders into GBCCF, milled in an agate mortar for 1 h. The obtained composite cathodes with different mass content of GDC: 10, 25 and 40% were named as GBCCF–GDC10, GBCCF–GDC25 and GBCCF–GDC40, respectively.

The electrical conductivity of the sintered sample GBCCF was measured by four-probe dc technique in the temperature range of 300–850 °C. TEC of GBCCF and GDC samples were measured using a dilatometer (NETZSCH DIL 402C) with an Al_2O_3 reference, which operated in a temperature range from 30 to 850 °C with an air purge flow rate of 60 ml min^{-1}.

The symmetrical cells were constructed with GDC electrolyte as the substrates to measure the interfacial polarization resistance. GBCCF and GBCCF–GDC electrodes were screen-printed onto both sides of the substrates and sintered at 950 °C for 2 h in air, respectively.

Phase analysis and crystal structures of the synthesized powders were evaluated using X-ray diffraction (XRD) (DX-2000 diffractometer) at room temperature. AC electrochemical impedance spectroscopy (EIS) was conducted by a Zaher Im6ex electrochemical workstation. The impedance of a symmetric cell was measured in ambient air, and typically in the frequency range of 1 MHz to 100 mHz with signal amplitude of 10 mV over a temperature range 650–800 °C.

3. Results and discussion

Fig. 1 shows the room temperature XRD pattern of GBCCF powders. Single-phase perovskite structure was formed when GBCCF was fired at 1000 °C for 10 h in air through intermediate grinding and calcining at 950 and 970 °C. For a comparison, the XRD date of the GBCC is also shown in Fig. 1. The GBCCF composition was crystallized in a single phase with layered perovskite structure, which agrees well with the data reported [11,17]. There is no detection of any additional diffraction peaks attributable to impurities.

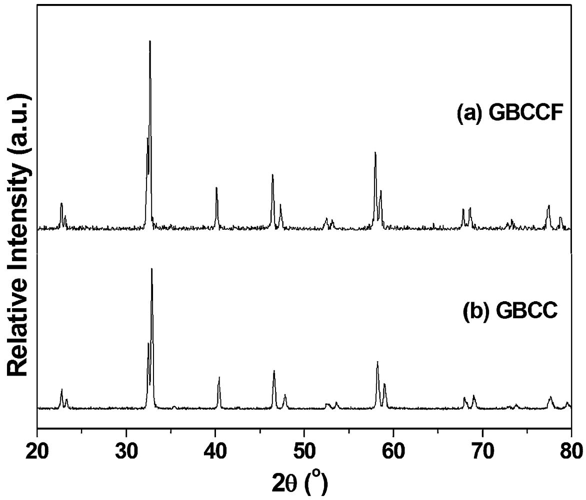

Fig. 1. XRD diffraction patterns of (a) $GdBaCuCo_{0.5}Fe_{0.5}O_{5+\delta}$ (GBCCF), (b) $GdBaCuCoO_{5+\delta}$ (GBCC). XRD data of sample GBCC were taken from Ref. [11].

Fig. 2 shows the conductivity of GBCCF in air as function of temperatures. The conductivity value of GBCCF sample in the working range of IT-SOFCs (650–800 °C) are 9–13 S cm^{-1}, which is a little bit lower than that of reported pure Co based cathode under the same conditions [11]. This may be due to the level of oxygen vacancy generation during heating is bigger in GBCCF sample. The oxygen and Co^{4+} ion content in GBCCF sample decreases and leads to the reduction of the carrier concentration and, consequently, this results a decrease in conductivity. The decrease in conductivity partial substitution of Fe for Co was also reported for the $LnBaCo_{2-x}Fe_xO_{5+\delta}$ (Ln = Nd and Gd) and $YBaCo_{2-x}Fe_xO_{5+\delta}$ systems [18,19]. The electrical conductivity of the sample GBCCF increases with the increasing temperature, exhibiting a semiconductor-like behavior, which is a feature of a heat-activated conducting mechanism. The inset in Fig. 2 shows the Arrhenius plot of GBCCF pellet. It can be described well by a small-polaron hopping model, following the formula: $\sigma = (A/T)\exp(-E_a/kT)$, where A is the material constant including the carrier concentration term, E_a the activation energy, k is the Boltzmann's constant and T is the absolute temperature. The activation energy is 28.84 kJ mol^{-1} calculated from the slope of the Arrhenius plot.

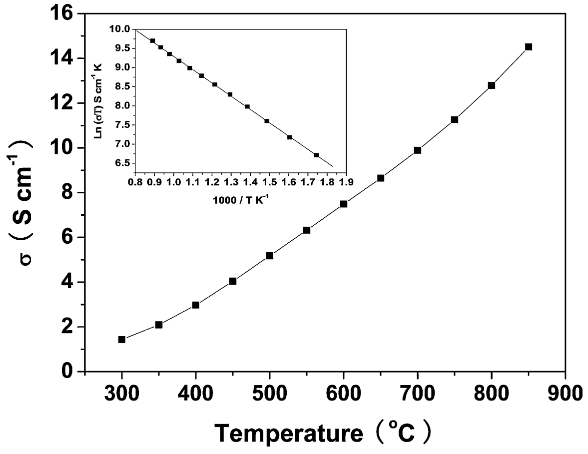

Fig. 2. Temperature dependence of the electrical conductivity for GBCCF sample. Inset shows ln σT vs. $1000/T$ plot.

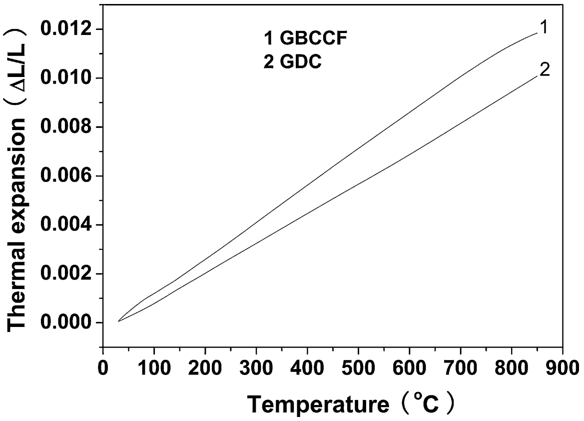

Fig. 3. Thermal expansion curves of sintered GBCCF cathode and GDC electrolyte in the temperature range of 30–850 °C in air.

As a cathode material for SOFCs, the TEC of the cathode should be close to other components of the cell. Fig. 3 shows the thermal expansion curves of GBCCF sample over a temperature range of 30–850 °C in air. To compare it fairly with GDC electrolyte, the thermal expansion curve of the GDC sample sintered at 1400 °C for 10 h in air is also shown in Fig. 3. Average TEC values of samples GBCCF and GDC are $14.4 \times 10^{-6}\,K^{-1}$ and $12.2 \times 10^{-6}\,K^{-1}$ in the temperature range of 30–850 °C, respectively. In addition, the TEC value of the GBCCF cathode is much lower than other cobaltite perovskite cathodes, such as $SmBaCuCoO_{5+\delta}$, $LnBaCo_2O_{5+\delta}$, and $SrCo_{1-y}Nb_yO_{3-\delta}$ [15,20,21]. Thus, partial substitution of Fe in the Co sites of GBCC can control the large thermal expansion. The thermal expansion behavior results show that GBCCF sample is structurally stable in the studied temperature range.

The electrochemical impedance spectra of symmetrical GBCCF/GDC/GBCCF testing cells under open-circuit condition are presented in Fig. 4. In these spectra, the intercept with the real axis at low frequencies represents the total cell resistance (R_t) and the value of the intercept at high frequency is ohmic resistance (R_o), while the difference of the two values corresponds to interfacial polarization resistance (R_p). The R_p significantly reduces with the increasing temperature. The R_p value was 2.720, 1.409, 0.650, and 0.330 Ω cm^2 at 650, 700, 750 and 800 °C, respectively, which is lower compared to $La_{0.9}Ca_{0.1}Ni_{0.5}Co_{0.5}O_3$ cathode [22].

To further optimize the electrochemical performance of GBCCF cathode, GDC is added to GBCCF to form GBCCF–GDC composite electrodes. The impedance spectra of

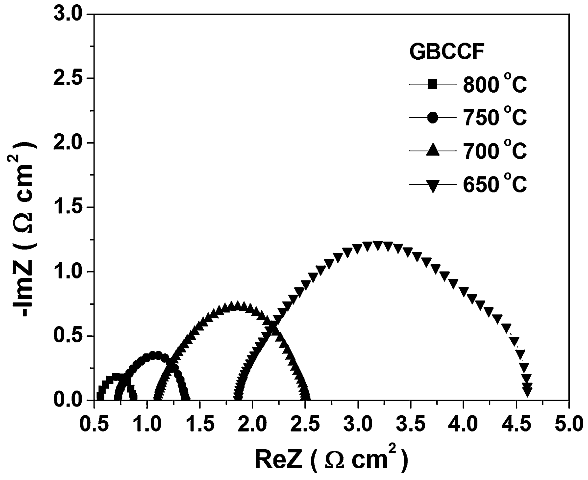

Fig. 4. Typical impedance spectra of GBCCF cathode on GDC electrolyte measured at 650–800 °C in air under open circuit conditions.

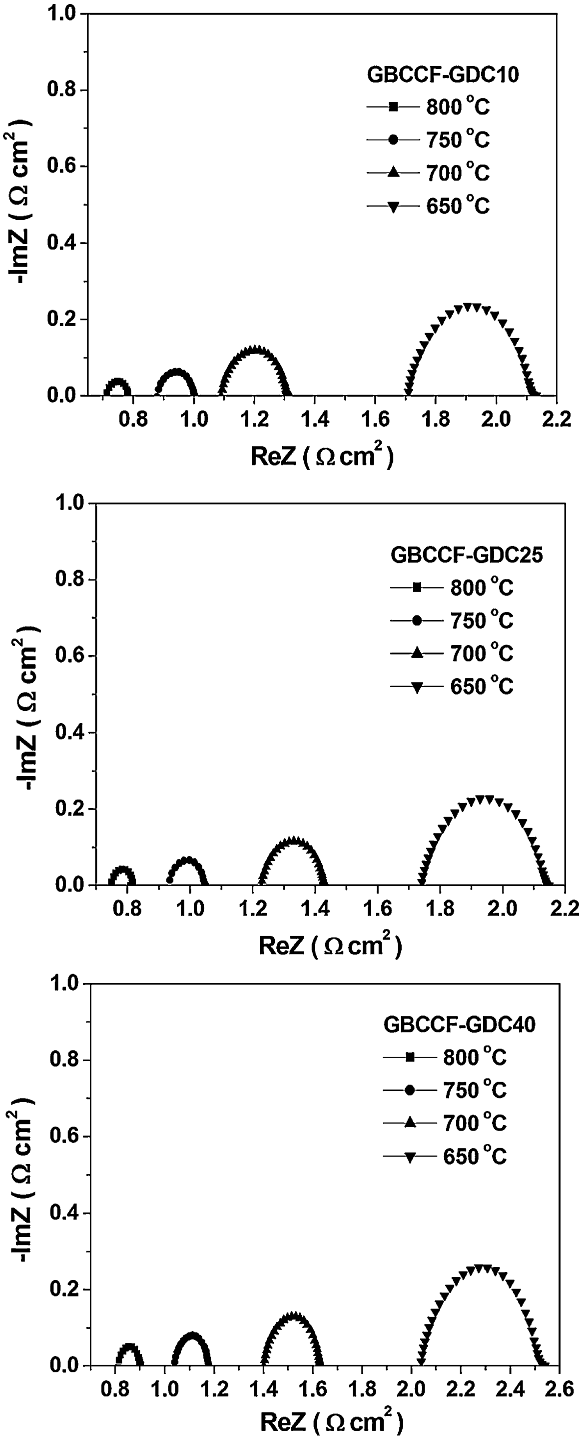

Fig. 5. Typical impedance spectra of GBCCF–GDC composite cathodes on GDC electrolyte measured at 650–800 °C in air under open circuit conditions.

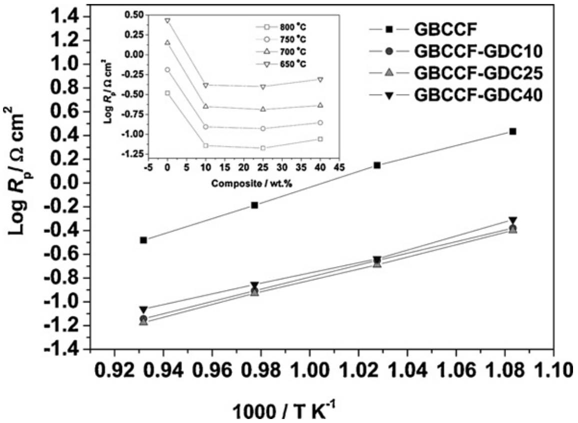

Fig. 6. Arrhenius plots of R_p from GBCCF and GBCCF–GDC composite electrodes as a function of temperature and GDC contents.

GBCCF–GDC10, GBCCF–GDC25, and GBCCF–GDC40 on GDC electrolyte pellets are shown in Fig. 5. Fig. 6 shows Arrhenius plot of the R_p values for GBCCF and GBCCF–GDC composite cathodes on the GDC electrolyte. It can be seen that the GDC content had a significant effect on the R_p of the electrodes. The GBCCF–GDC25 exhibits the smallest R_p among the GBCCF–GDC composite cathode, where the values are only about 0.067, 0.118, 0.205, and 0.399 Ω cm^2 at 800, 750, 700 and 650 °C, respectively, which is much lower that those of pure GBCCF cathode at the corresponding temperatures. However, as GDC content further increases to 40%, R_p increases. Addition of GDC to GBCCF is effective in improving the electrocatalytic activity of cathode due to enlargement of the electrochemically active area, i.e., the triple phase boundary (TPB), at which the oxygen reduction reaction occurs. However, too much GDC obstructs the connections between GBCCF particles, thus decreasing the effective TPBs and electrical conductivity.

4. Conclusions

The cathode performance of GBCCF was investigated for potential application in IT-SOFCs. The average TEC of GBCCF was 14.4×10^{-6} K^{-1} in the temperature range of 30–850 °C in air. The cathode performance was also studied by contrasting the interfacial resistance of the single-phase GBCCF and its composite with GDC. The best performance was achieved by the composition GBCCF–GDC25 with an R_p value as low as 0.118 Ω cm^2 at 750 °C measured on GDC electrolyte. These results allow us to propose that the GBCCF cathode is a good candidate for IT-SOFCs, whose stability and performance on single cell will be investigated in the future.

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