Evaluation of GdBaCuCo$_{0.5}$Fe$_{0.5}$O$_{5+\delta}$ as cathode material for intermediate temperature solid oxide fuel cells

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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.
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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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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$_2$O$_3$ (99.99%), BaCO$_3$ (99%), CuO (99%), Co$_3$O$_4$ (99%), Fe$_2$O$_3$ (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$_2$O$_3$ 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. 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
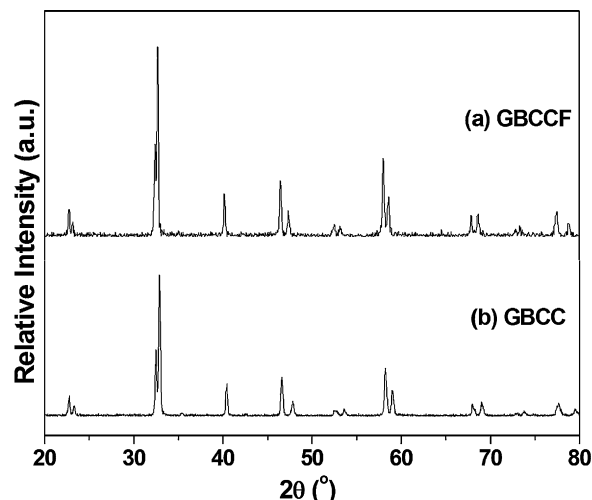

Fig. 1. XRD diffraction patterns of (a) GdBaCuCo$_{0.5}$Fe$_{0.5}$O$_{5+\delta}$ (GBCCF), (b) GdBaCuCoO$_{5+\delta}$ (GBCC). XRD data of sample GBCC were taken from Ref. [11].

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$_x$O$_{5+\delta}$ (Ln = Nd and Gd) and YBaCo$_{2-x}$Fe$_x$O$_{5+\delta}$ 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.
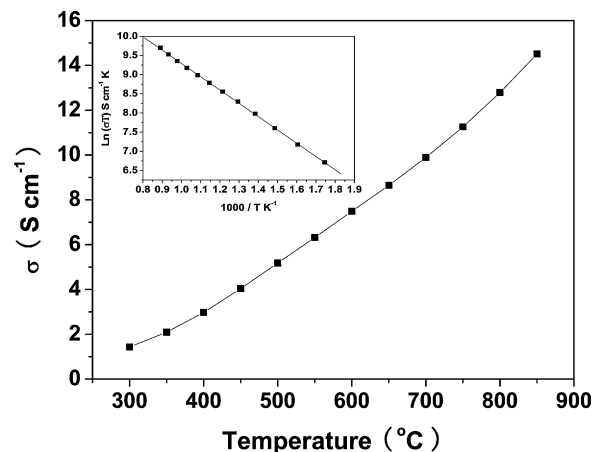

Fig. 2. Temperature dependence of the electrical conductivity for GBCCF sample. Inset shows ln σT vs. 1000/T plot.