Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 1529–1532

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

$LaBaCuFeO_{5+\delta}$–$Ce_{0.8}Sm_{0.2}O_{1.9}$ as composite cathode for solid oxide fuel cells

Qingjun Zhou *, Wei Wang, Tong Wei, Xuelian Qi, Yan Li,
Yunling Zou, Ye Liu, Zepeng Li, Yao Wu

College of Science, Civil Aviation University of China, Tianjin 300300, PR China

Received 5 September 2011; received in revised form 17 September 2011; accepted 17 September 2011
Available online 22 September 2011

Abstract

The performance of the $LaBaCuFeO_{5+\delta}$–$Ce_{0.8}Sm_{0.2}O_{1.9}$ (LBCF–SDC) composite cathodes was studied in this paper. Electrical conductivity, thermal expansion and electrochemical properties were investigated by four probing DC technique, dilatometry, AC impedance and polarization techniques, respectively. The thermal expansion coefficients of the LBCF–SDC were between (16.3 and 13.4) $\times 10^{-6}$ K^{-1} from 30 to 850 °C, which was lower value than LBCF (17.0×10^{-6} K^{-1}). AC Impedance spectroscopy measurements of LBCF–SDC/SDC/LBCF–SDC test cell were carried out. Polarization resistance values for the LBCF–SDC10 cathode was as low as 0.097 Ω cm^2 at 750 °C.

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

1. Introduction

Solid oxide fuel cell (SOFC) is all-solid electrochemical device which converts chemical energy directly into electric power with high conversion efficiency and low to zero emission [1]. Recently, the development of intermediate-temperature solid oxide fuel cells (IT-SOFCs) is considered to be a realistic approach to practical application and commercialization [2–4]. However, the electrochemical activity of the cathode dramatically decreases with decreasing temperature. At lower temperatures, the cathode becomes the limiting factor in determining the overall cell performance. Therefore, the development of new electrodes with high-electrocatalytic activity for the oxygen-reduction reaction is crucial to achieve a favorable cell performance at intermediate temperature range (600–800 °C).

Recently, a family of oxides such as $LnBaCuMO_{5+\delta}$ (Ln = rare earth, M = Co, Fe) with the layered perovskite-type structure has drawn much attention for its potential application as IT-SOFCs cathode [5–12]. The preliminary results showed that the layered perovskite structure oxides $LnBaCuMO_{5+\delta}$ are very promising candidates as cathode materials for application in IT-SOFCs. However, to our best knowledge, when the Co occupying the B-sites, often suffer from some problems like high thermal expansion coefficients (TEC), poor stability and high cost of cobalt element. It is desirable to develop the cobalt-free cathodes with good electrocatalytic activity for IT-SOFCs. Therefore, in order to reduce disadvantages and improve the performance, much attention should be paid to cobalt-free layered perovskite cathode.

In this study, we systematically investigated the performance of $LaBaCuFeO_{5+\delta}$. Our aim was to improve the electrochemical performance and reduce TEC mismatch between cathode and electrolyte. The LBCF–SDC composite cathodes were investigated by X-ray diffraction, electrical conductivity, thermal expansion coefficient measurements and electrochemical impedance spectroscopy technique.

2. Experimental procedures

The $LaBaCuFeO_{5+\delta}$ (LBCF) oxide was synthesized by conventional solid-state reaction methods. Stoichiometric amounts of commercial powders La_2O_3 (99.99%), $BaCO_3$ (99%), CuO (99%), and Fe_2O_3 (99.5%) were ground thoroughly with ethanol as grinding medium using an agate

---

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

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.09.037

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. SDC powders were synthesized with the glycine–nitrate process described elsewhere [13]. The obtained LBCF powder was mixed with different amounts of SDC powder (0–50 wt%) to make composite cathodes (denoted here by "LBCF–SDC*x*", $x = 0$, 10, 20, 30, 40, and 50). These LBCF–SDC*x* powders were pressed into pellets followed by sintering at 950 °C for 2 h. The sintered pellets were used for the electrical conductivity and the TEC measurements. The cathode powders were mixed with ethylcellulose and terpineol to obtain well-distributed cathode slurry. LBCF–SDC*x* electrodes were screen-printed onto both sides of the SDC electrolytes and sintered at 950 °C for 2 h in air, respectively.

X-ray diffraction (DX-2000) was used to confirm the crystalline structure of the prepared powders. The electrical conductivities of sintered LBCF–SDC*x* pellets were measured using the four probing DC technique. The TEC for each LBCF–SDC*x* samples was measured using a Netzsch DIL 402C dilatometer, which operated in a temperature range from 30 to 850 °C with an air purge flow rate of 60 ml min^{-1}. AC impedance spectroscopy of the symmetrical cell was tested under open-circuit conditions using an electrochemical impedance spectrum analyzer (Zaher Im6ex). The frequency range was 0.1 Hz to 1 MHz with signal amplitude of 10 mV over a temperature range 650–800 °C. Morphologies of the cathode after electrochemical test were characterized by a scanning electron microscope (SEM, JSM-6480LV, JEOL, Japan).

3. Results and discussion

Fig. 1 shows the XRD patterns of 50 wt% LBCF–50 wt% SDC mixtures calcined at 950 °C for 2 h. For comparison, the patterns of LBCF and SDC powders are also shown in the same figure. After the LBCF–SDC mixture was sintered at 950 °C, LBCF and SDC retained their own structures, respectively. No reaction products were detected by XRD. It seems that LBCF cathode is chemically compatible with the SDC electrolyte for temperatures up to 950 °C for 2 h.

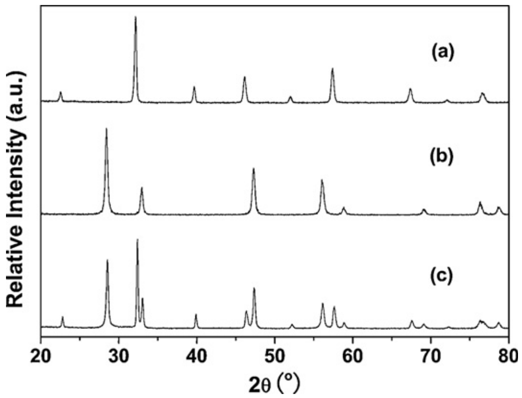

Fig. 1. X-ray diffraction patterns of (a) LBCF, (b) SDC and (c) LBCF–SDC composites sintered at 950 °C for 2h.

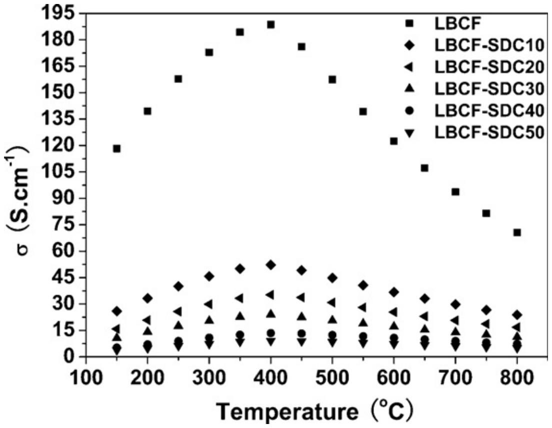

Fig. 2. Temperature dependence of the electrical conductivity of The LBCF–SDCx samples with different SDC contents in air. Conductivity data of sample LBCF were taken from Ref. [6].

Fig. 2 shows the temperature dependence of the electrical conductivities of LBCF–SDC samples with different SDC contents measured in air. It can be seen that there is an abrupt change of slope at around 400 °C, which undergoes from a semiconducting-like conduction behavior to metal-like conduction behavior. The Arrhenius plots of conductivity of LBCF–SDC*x* are presented in Fig. 2. As can be seen, the Arrhenius plots of conductivity are nearly linear in low temperature range (<400 °C), i.e., the conductivity (σ) dependence of temperature (T) can be expressed as

$$\sigma = \left(\frac{A}{T}\right)\exp\left(\frac{-Ea}{kT}\right) \qquad (1)$$

where A is the pre-exponential constant, k is the Boltzmann constant, T is the absolute temperature, and Ea is activation energy of the electrical conductivity. By introducing SDC as the second phase, a drop in electrical conductivity was observed, where higher amounts of SDC resulted in a decrease in conductivity.

Fig. 3 shows the thermal expansion curves of LBCC–SDC*x* and SDC samples in the temperature range of 30–850 °C in air. Specific TEC values were presented in Table 1. As can be seen, compared with the TEC of LBCF, the TEC of LBCF–SDC

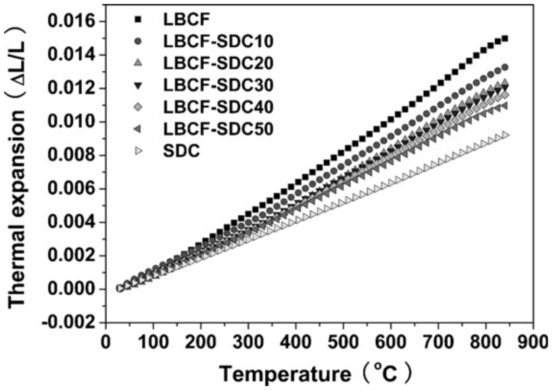

Fig. 3. Thermal expansion curves of composite cathodes in the temperature range of 30–850 °C in air.