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Effect of Bi_2O_3 on the electrochemical performance of $LaBaCo_2O_{5+\delta}$ cathode for intermediate-temperature solid oxide fuel cells

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Abstract

The $LaBaCo_2O_{5+\delta}-x$ wt.% Bi_2O_3 (LBCO-$x$$Bi_2O_3$, $x=10$, 20, 30, and 40) were prepared as composite cathodes for intermediate-temperature solid oxide fuel cells (IT-SOFCs) via the conventional mechanical mixing method. The effect of Bi_2O_3 on polarization resistance, overpotential, and long-term stability of the LBCO cathode was investigated. An effective sintering aid for LBCO cathode, Bi_2O_3 not only lowers its sintering temperature by $\sim$200 °C, but also improves the electrochemical performance within the intermediate temperature range of 600–800 °C. Electrochemical impedance spectroscopy measurements showed that the addition of 20 wt% Bi_2O_3 to LBCO exhibited the lowest area-specific resistance of 0.020 Ω cm^2 at 800 °C in air, which was about a seventh of that of the LBCO cathode at the same condition. At a current density of 0.2 A cm^{-2}, the cathodic overpotential of LBCO-20Bi_2O_3 was about 12.6 mV at 700 °C, while the corresponding value for LBCO was 51.0 mV. Compared to B_2O_3–Bi_2O_3–PbO frit, the addition of Bi_2O_3 significantly improved the long-term stability of cathode. Therefore, LBCO-20Bi_2O_3 can be a promising cathode for IT-SOFCs.

Keywords: A. Mixing; B. Microstructure; C. Impedance; E. Fuel cells

1. Introduction

As an all-solid-state electrochemical system, solid oxide fuel cells (SOFCs) can directly convert the chemical energy of fuel into electricity in an efficient and clean way, which usually operated at temperatures as high as 1000 °C [1–4]. Lowering their operating temperature to an intermediate temperature range of 600–800 °C has been widely investigated in recent years, and this process is considered as a very promising method to widen the practical application of SOFCs [5–11]. However, the cathodic electrochemical performance decreases with decreasing operating temperature, which directly affects the overall performance of the system [4,11–14]. Therefore, the development of high-performance cathodes with low polarization losses, high electrocatalytic activity for oxide reduction reaction, and good long-term stability within the intermediate temperature range has become increasingly critical.

Our previous study [14,15] proved that the B_2O_3–Bi_2O_3–PbO frit is proved to be effective in lowering the sintering temperature of $LaBaCo_2O_{5+\delta}-x$ wt.% Ag and $LaBaCo_2O_{5+\delta}$ cathodes and in improving their electrochemical performance within the intermediate temperature range. However, the long-term stability of these composite cathodes poses a challenge because of the relatively low melting temperature of B_2O_3–Bi_2O_3–PbO frit ($\sim$550 °C). Moreover, the use of Pb, especially at such high temperatures, is not recommended given the worsening pollution in the environment.

Therefore, looking for new sintering aids for the cathode is important. The key factor determining a material could be used as sintering aid is considered that the material should be able to lower the sintering temperature of cathode without sacrificing the performance (mainly including electrochemical performance and long-term stability), maintain the structural stability within an intermediate temperature range, cause no damage to the porous structure of the cathode, and have good chemical compatibility with other components.

Based on the above mentioned considerations, Bi_2O_3 was chosen as the sintering aid for $LaBaCo_2O_{5+\delta}$ cathode for IT-SOFCs in this study. As a good ionic conductor, Bi_2O_3 has been investigated as a potential oxide ion-conducting solid electrolyte for SOFCs [16–18]. The melting point of Bi_2O_3 is about 825 °C, making it can remain the structural stability

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within intermediate temperature range of 600–800 °C. Attempts were made to investigate the effects of Bi_2O_3 on the polarization resistance, cathodic overpotential, and long-term stability of $LaBaCo_2O_{5+\delta}$ cathode via AC impedance and cyclic voltammetry (CV) techniques.

2. Experimental

La_2O_3 (99.9%), $BaCO_3$ (99.0%), Co_2O_3 (99.0%), Sm_2O_3 (99.99%), and CeO_2 (99.99%) were used as starting materials. The detailed synthetic process of $LaBaCo_2O_{5+\delta}$ (LBCO) cathode and $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte powders, and the preparation of dense SDC pellets were described in our previous study [15].

LBCO and Bi_2O_3 (99.0%) powder was mixed with an appropriate mass ratio of ethyl cellulose and terpinol, which was painted via the screen painting method onto both sides of the SDC pellets with a circle pattern (about 10 mm diameter) and then calcined at 900 °C in air. The current collector, Ag paste, was painted onto the cathode surface and calcined at 770 °C.

The electrochemical impedance spectroscopy (EIS) were performed using PARSTAT 2273 electrochemical workstation under open circuit voltage from 600 °C to 800 °C in air, and with excitation potentials of 10 mV and frequency range of 100 kHz–0.1 Hz. The impedance spectra were fitted and analyzed using the ZsimpWin software. The polarization analysis was carried out on a three-electrode cell at 700 °C. As reference electrode, Ag paste was prepared with a ring shape, to ensure a sufficient distance between the Ag paste and the working electrode (at least twice the thickness of the SDC electrolyte).

The long-term stability of the cathode was also characterized via EIS. The impedance spectra of the same cathode sample before and after 3000 min of aging at 800 °C in air were compared with each other to evaluate the cathode stability. Moreover, the microstructure was characterized by scanning electron microscopy (SEM, JEOL, JSM-5900, Tokyo, Japan). To avoid electrostatic effect, the surface of the sample was coated with gold before the test.

3. Results and discussion

3.1. Crystal structure and chemical compatibility

To investigate the phase reaction between the cathode and Bi_2O_3, the mixed powders consisting of LBCO and 20 wt% Bi_2O_3 were calcined at 800 °C for 2 h and 3000 min in air. As shown in Fig. 1, $La_{0.19}Bi_{0.81}O_{1.5}$ and bismuth oxide were observed at 2θ values between about 26 °C and 30 °C, whereas the LBCO structure remained unchanged. The peak height of the new phases hardly changed after 3000 min of aging at 800 °C. The influence of all the new phases on the cathode performance is considered to be negligible because of their little content and relatively random distribution.

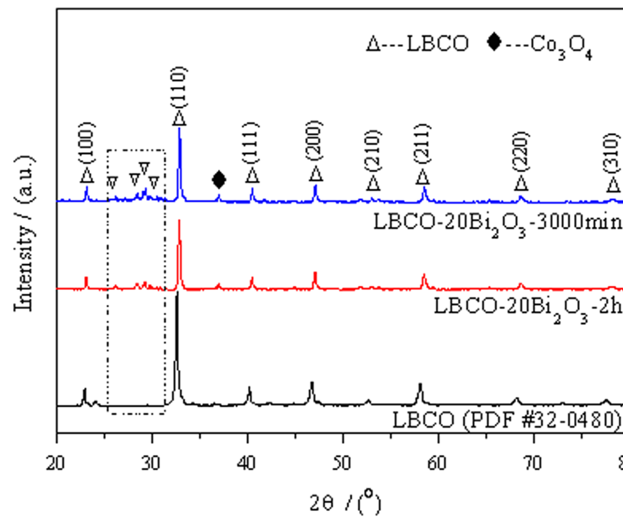

Fig. 1. XRD patterns of the LBCO cathode calcined at 1100 °C for 2 h and LBCO-20 Bi_2O_3 calcined at 800 °C for 2 h and 3000 min.

3.2. Electrochemical impedance spectroscopy

Fig. 2 shows the AC impedance spectra of LBCO-$x$$Bi_2O_3$ cathodes measured at 700 °C and 800 °C in air. The impedance spectra were fitted to the equivalent circuit $LR_{ohm}(R_pQ)$, where L is the high-frequency inductance, R_{ohm} is the ohmic resistance, R_p is the polarization resistance and corresponds to the differences between real-axes intercepts, and Q is the corresponding constant phase elements. For simplification, LBCO-$x$$Bi_2O_3$ (x=10, 20, 30, and 40 wt%) is the LBCO cathode with different amounts of Bi_2O_3, and x denotes the Bi_2O_3 fraction in the LBCO-$x$$Bi_2O_3$ mixed powder.

As shown in Fig. 2, the R_p of LBCO-$x$$Bi_2O_3$ first decreased at each measured temperature, reached the minimum at 20 wt% Bi_2O_3, and then increased with increasing Bi_2O_3 content. This tendency can be explained as follows: when the Bi_2O_3 content is about 10 wt%, LBCO-10Bi_2O_3 can hardly form a relatively dense cathode functional layer after sintering at 900 °C (the sintering temperature of LBCO is about 1100 °C in air [15]), and a high R_p was observed. For LBCO-20 Bi_2O_3, the improved performance can be attributed to the optimized microstructure and the high ionic conductivity of Bi_2O_3. An appropriate amount of Bi_2O_3 (~20 wt%) makes the LBCO-$x$$Bi_2O_3$ sample after sintering at 900 °C to form a optimum structure with reasonable porosity and shows good adhesion to SDC electrolyte. In addition, with the addition of high ionic conductive Bi_2O_3, the triple phase boundary (TPB) areas were extended to the whole cathode layer, resulting in an improvement in the electrochemical performance. However, when the Bi_2O_3 content was increased above 30 wt%, the excessive amount of Bi_2O_3 makes the LBCO-$x$$Bi_2O_3$ sample to form a too dense structure (not beneficial for the transport of the electron and gas), leading to a sharp increase of R_p.

The area-specific resistance (ASR) of the cathode is the size-related parameter based on the geometric area of the cathode and the polarization resistance R_p. The R_p of a single cathode is half that of the obtained R_p in Fig. 2 because the two-electrode configuration was used in our experiments. Therefore, the ASR value is defined as follows:

$$ASR = \frac{R_P}{2} \times \text{cathode area} \quad (1)$$