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Functionally graded cathodes based on double perovskite type $GdBaCo_2O_{5+\delta}$ oxide

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ABSTRACT

Large thermal mismatch between $GdBaCo_2O_{5+\delta}$ (GBCO) oxide and solid electrolytes remains a challenge for its application as a cathode of solid oxide fuel cells (SOFCs). To avoid sharp discontinuities in composition, a functionally graded GBCO cathode is developed, which consists of an inner layer with high electrochemical activity and good thermal compatibility to electrolyte, and an outer layer with high electrical conductivity for current collection. Impedance spectra results reveal that the graded GBCO cathode shows a reduced polarization resistance and more importantly, an improved thermal stability during thermal cycling test. The present work confirms the advantage of graded GBCO cathode that is more robust and reliable for practical application.

1. Introduction

Solid oxide fuel cells (SOFCs) are widely considered as a promising technique for future power generation, due to its high energy conversion efficiency, quite low polluted emission and excellent fuel flexibility [1]. Currently, reducing the operation temperature to intermediate temperature (≤800 °C, i.e., IT-SOFCs) is critical for the commercialization. $La_{1-x}Sr_xMnO_3$ perovskite oxide (LSM) is extensively used as a state-of-the-art cathode for SOFCs, because of its high thermal and chemical stability [2]. In general, LSM cathode exhibits satisfactory performance at above 800 °C. But with the decrease of temperature, the cathodic polarization resistance will increase rapidly, due to its low oxygen ion conductivity and high activation energy for oxygen reduction reactions (ORR). Therefore, it is very important to develop high performance cathode for IT-SOFCs.

Great efforts have been made to develop the perovskite-type mixed ionic and electronic conductors (MIECs), like $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [3,4], $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ [5,6] (SSC) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [7–10] oxides. These MIECs often demonstrate higher oxygen-ion conductivity, electronic conductivity and electro-catalytic activity, making them very attractive for cathodes of reduced temperature SOFCs. Recently, double perovskite oxides $LnBaCo_2O_{5+\delta}$ (Ln = Pr, Nd, Sm, Gd...) [11–17] with A-site cation ordered structure have attracted extensive interests. Very fast oxygen-ion transport and surface exchange properties make them exhibit excellent electrochemical activity towards ORR at intermediate temperatures. But unfortunately, these cobalt-based cathodes also suffer from a serious problem of high thermal expansion coefficients (TECs). Typically, the TEC values of these double perovskite oxides are around $20 \times 10^{-6}K^{-1}$ [14,18], which are significantly larger than that of YSZ and ceria based electrolytes ($10\sim13 \times 10^{-6}K^{-1}$) [19,20]. Such a great thermal mismatch will lead to poor thermal compatibility with electrolytes, especially during multiple thermal cycles.

This problem can be alleviated by tailoring the cathode microstructure. One strategy to effectively cure the mismatch is the adoption of a functionally graded design that can avoid the undesired sharp discontinuity in TECs [21–28]. These graded cathodes are characterized with an inner electrochemically active layer and an outer current collecting layer. Moreover, Liu et al. have proposed an ideal structure with both composition and porosity gradients, which consists of fine grains (high surface area) close to the electrolyte surface, and large grains (large pore size) at air side [29]. Ni et al. have developed a mathematical model to describe the effect of microstructurally graded electrode on the SOFC performance, which reveals that both porosity and particle size gradients are effective to improve SOFC performance [30].

For $GdBaCo_2O_{5+\delta}$ (GBCO)-ceria based composite cathodes, previous results show that both thermal mechanical and electrochemical properties are improved, but the electrical conductivity is also lowered with the increasing content of $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC)

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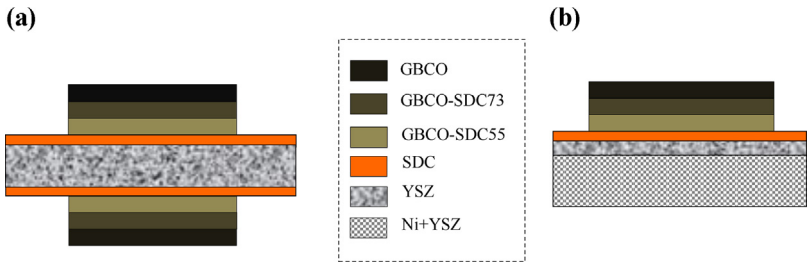

Fig. 1. Schematic illustrations for (a) symmetrical half-cell and (b) anode supported fuel cell.

[31]. In order to improve the cathode thermal compatibility and electrochemical activity while remain high electronic conductivity, a functionally graded GBCO cathode is proposed and studied in this study. The performance of the graded GBCO cathode is compared with a pure GBCO cathode. Our results reveal that the graded GBCO cathode demonstrates greatly reduced polarization resistance and enhanced thermal tolerance to thermal cycling.

2. Experimental

2.1. Materials synthesis

The synthesis procedures of $GdBaCo_2O_{5+\delta}$ and $Ce_{0.8}Sm_{0.2}O_{1.9}$ powders were briefly introduced below. $GdBaCo_2O_{5+\delta}$ oxide powder was prepared by a complexing sol-gel process using both ethylenediamine tetraacetic acid (EDTA) and citrate as complexing agents. Gd_2O_3, $Ba(NO_3)_2$, $Co(NO_3)_2{\cdot}H_2O$, EDTA, $NH_3{\cdot}H_2O$ and citric acid (all in analytical grade) were used as raw materials. A mole ratio of 1:1:2 for total metal ions:EDTA:citric acid was used. Firstly, Gd_2O_3 was dissolved in nitric acid that kept in a water bath at 80 °C. EDTA-$NH_3{\cdot}H_2O$ solution, rest metal nitrates and citric acid were subsequently added and mixed under continuous stirring. Then, the *p*H value of the solution was adjusted to ~7 using ammonia water. With the evaporating of water, a purple viscous gel was obtained. Then the gel was pre-heated at 200 °C in an oven for 10 h and followed by calcination at 1000 °C for 4 h to yield the black GBCO oxide powder. For $Ce_{0.8}Sm_{0.2}O_{1.9}$ preparation, only citrate was exploited as a complexing agent, and the mole ratio of total metal ions: citrate was controlled as 1:1.5. Stoichiometric amount of Sm_2O_3 was dissolved in hot nitric acid at 80 °C, $Ce(NO_3){\cdot}6H_2O$ and citrate were then introduced. Evaporation of water and pre-heating at 100 °C for 10 h resulted in brown precursor, which was further calcinated at 800 °C for 2 h to obtain the SDC powder. To check the phase purities, as-prepared GBCO and SDC powders were examined by an X-ray diffractometer (XRD, Rigaku D/max-rB, Japan) and the results confirmed that they have formed desired phases.

2.2. Symmetrical half-cell fabrication

To prepare the electrolyte substrate, 0.25 g 8YSZ powder (TZ8Y, Tosoh, Japan) was pressed under ~200 MPa, then a coarse YSZ layer was prepared via slurry coating method to increase the surface roughness. These pellets were sintered at 1400 °C for 4 h. It is reported that GBCO can readily react with YSZ electrolyte[15], while GBCO and SDC shows a reasonable chemical compatibility. Therefore, an SDC protective layer is desired between GBCO and YSZ to prevent their direct contact. Through a spin coating technique, SDC ink was deposited on both surfaces of YSZ pellets and sintered at 1300 °C for 1 h.

Organic additive consisting of 5 wt.% ethyl cellulose and terpineol was mixed with specific powder to prepare the colloidal cathode slurries. For functionally grade cathode, three kinds of cathode slurries were prepared, i.e. pure GBCO, GBCO-SDC73 (containing 30 wt.% SDC) and GBCO-SDC55(containing 50 wt.% SDC). By a screen-printing technique, GBCO-SDC55 ink was first applied onto SDC surfaces. After drying, similar deposition of GBCO-SDC73 and pure GBCO inks were carried out in sequence. Finally, the circular graded cathode with an effective area of 0.28 cm^2 was sintered at 950 °C for 4 h. A schematic picture of symmetrical half-cell is given in Fig. 1a. A similar half-cell with pure GBCO cathode was also fabricated for comparison.

2.3. Single cell fabrication

Anode powders of YSZ, NiO (Inco, Canada) and starch in a weight ratio of 50:50:20 were mixed in a mortar for 1 h. The mixed powder was pressed into pellets and pre-calcinated at 1000 °C for 2 h. Then, a thin YSZ film was deposited on as-prepared NiO + YSZ anode support by a slurry spin-coating method. After co-sintering of the anode/electrolyte bilayer at 1400 °C for 4 h, an SDC layer was further prepared and sintered at 1300 °C for 1 h. Finally, the graded GBCO cathode was screen-printed on SDC surface and sintered at 950 °C for 4 h, forming a complete single cell, as schematically shown in Fig. 1b.

2.4. Characterizations

The electrochemical performances of both half-cells and single cell were tested by an electrochemical workstation (Biologic VSP, France) using a two-electrode four-wire configuration. These tests were performed between 600 °C and 850 °C. Impedance spectra were collected in a frequency range of 100 kHz ~ 0.1 Hz under open-circuit condition with a signal amplitude of 10 mV. A Zview 2.3f software (Scribner Associates) was used for impedance spectra fitting. For fuel cell performance evaluation, a mixture of 50%H_2 + 50%Ar at a fixed flow rate of 150mL·min^{-1} was fed to the anode chamber, while the cathode side was exposed to stationary air. After testing, the microstructure and composition of half-cell or single cell were observed by a scanning electron microscope (SEM, Zeiss LEO 1530 Gemini, Germany) equipped with an Energy Dispersive X-Ray Spectrometer (EDX).

3. Results and Discussion

3.1. Symmetrical half-cells performance

The electrochemical performance of graded GBCO cathode was first tested as a function of operating temperature. A pure GBCO cathode was also measured for comparison. Typical impedance spectra obtained at 800 °C are given in Fig. 2a for graded GBCO and pure GBCO cathodes. These spectra were fitted using an equivalent circuit given in Fig. 2b, and the fitting parameters are listed in Table 1. Here, *L* is the inductance that is attributed to the silver current–voltage leads or the high-frequency phase shift of electrochemical equipment, *Ro* is the ohmic resistance mainly including the electrolyte resistances from YSZ and SDC barrier layer and