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Conductivity and electrochemical performance of $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ cathode prepared by the citrate–EDTA complexing method

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Abstract

This study reports the successful preparation of single-phase perovskite $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ ($x = 0$–0.2) by the citrate–EDTA complexing method. The crystal structure, thermal gravity analysis, coefficient of thermal expansion, electrical conductivity, and electrochemical performance of $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ were investigated to determine its suitability as a cathode material for intermediate-temperature solid oxide fuel cells (IT-SOFCs). The lattice parameter a of $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ decreases as the amount of Mn doping increases. The coefficients of thermal expansion of the samples are in the range of 21.6–25.9 $\times 10^{-6}\,K^{-1}$ and show an abnormal expansion at around 400 °C associated with the loss of lattice oxygen. The electrical conductivity of the $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ samples decreases as the amount of Mn-doping increases. The electrical conductivity of the samples reaches a maximum value at around 400 °C and then decreases as the temperature increases. The charge transfer resistance, diffusion resistance and total resistance of a $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{0.8}Mn_{0.15}O_{3-\delta}$–$Ce_{0.8}Sm_{0.2}O_{1.9}$ composite cathode electrode at 800 °C are 0.11 $\Omega\,cm^2$, 0.24 $\Omega\,cm^2$ and 0.35 $\Omega\,cm^2$, respectively.

Keywords: Perovskites; Electrical properties; Impedance; Defects; Precursors-organic

1. Introduction

Solid oxide fuel cells (SOFCs) efficiently convert chemical energy into electricity in a silent and environmentally friendly manner. The SOFCs have many advantages, such as high power density, low pollution and fuel flexibility when using hydrocarbon fuels.[1–3] However, the high operating temperatures of SOFCs result in poisoning of the cathode by chromium species from Cr-based metallic interconnector and material compatibility between the electrolyte, electrode and interconnector is a challenge.[4] However, as the operating temperature of SOFCs decreases to an intermediate temperature range of 600–800 °C, the activation polarization of the cathode electrode clearly increases and the electrical conductivity and electrochemical performance of the cathode decrease. Therefore, it is important to develop a new high performance cathode material with low active polarization for intermediate-temperature SOFCs (IT-SOFCs).

Cobalt or iron-based perovskite cathode materials are known to exhibit higher ionic and electronic conductivities than other kinds of cathode materials, but they also have many disadvantages, such as a high coefficient of thermal expansion (CTE), the high cost of cobalt, and the easy evaporation and reduction of cobalt, which must be resolved.[5–8] The CTE of the cobalt-based ($\sim 20 \times 10^{-6}\,K^{-1}$) cathodes is much higher than that of the manganese-based cathode materials ($\sim 11 \times 10^{-6}\,K^{-1}$) due to the formation of oxygen vacancies, spin-state transitions associated with Co^{3+}, and the relatively weaker Co–O bond as compared with the Mn–O bond.[9–11] Iron-based perovskite cathodes have the advantage of electron or hole mobility and a low thermal expansion coefficient. Zhao reported a high power density SOFC of 718 mW/cm^2

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using $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ as cathode electrode. The conductivity of $Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ is 57 S/cm at 600 °C.[12] Therefore, iron-based perovskite materials may be a good candidate cathode for IT-SOFCs.

Recently, the citrate–EDTA complexing method had been widely used to prepare the SOFC cathode materials, such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $Ba_{0.6}Sr_{0.4}Co_{0.9}Nb_{0.1}O_{3-\delta}$ and $La_{0.6}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF).[13–16,18,19,21] The cathode powder prepared from citrate–EDTA complexing method exhibits many advantages such as homogeneous element distribution, high specific surface area, nano-crystallite and low temperature synthesis, therefore, a cathode made by this method can have better electrochemical properties. In this study, $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ ($x = 0.0$–0.20) was prepared by a citrate–EDTA complexing method, which enabled the formation of single-phase perovskite oxide. The crystal structure, lattice oxygen loss, coefficient of thermal expansion, electrical conductivity, and electrochemical performance of samples were investigated in detail.

2. Experiment

$(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ (BSLFMn) powders were prepared using the citrate–EDTA complexing method.[13–15] First, ethylenediaminetetraacetic acid (EDTA, Riedel-dehaen, 98%) was mixed with 6 M NH_4OH to form an NH_3–EDTA solution. Then, $Ba(NO_3)_2$ (J.T. Baker, 99.6%) and $La(NO_3)_3{\cdot}6H_2O$ (Alfa Aesar, 99.0%) were added, and the mixture was heated and stirred. $Sr(NO_3)_2$ (Alfa Aesar, 99.0%), $Mn(NO_3)_2{\cdot}4H_2O$ (Fluka, 99.0%) and $Fe(NO_3)_2{\cdot}6H_2O$ (J.T. Baker, 99.8%) were dissolved in another 6M NH_4OH solution. These two solutions were mixed and stirred before citric acid was added. The resulting molar ratio of EDTA:citric acid:total metal ions was 1:1.5:1. The pH was adjusted to 6 by adding a further 6 M of NH_4OH solution. The final solution was heated to 100 °C on a hotplate and stirred until water evaporated from it, leaving behind a sticky gel. This gel was then further heated at 200 °C for 3 h, calcined at 950 °C for 9 h, and sintered at 1050 °C for 5 h. The samples with different Fe/Mn ratios were designated as BSLFMn00, BSLFMn05, BSLFMn10, BSLFMn15 and BSLFMn20.

The structure of the $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ powders was determined using a powder diffractometer (LabX, XRD-6000) with Ni-filtered Cu Kα radiation and a diffraction angle scanning from 20° to 85° with a step of 0.01° and a rate of 1° min^{-1}. The electrical conductivity was measured in air using a DC four-terminal method using Agilent Technologies 34970A and 6645A data acquisition/switch units with silver as the metal electrode and wire. Thermogravimetry analysis (TGA) was performed between 30 °C and 1000 °C at a heating rate of 5 °C/min in N_2, air and O_2 using TA Instruments SDT-Q600 DSC-TGA. The coefficient of thermal expansion (CTE) was measured between 50 °C and 1000 °C using a Seiko Instruments TMA/SS 6100 dilatometer with a heating rate of 5 °C/min in air. BSLFMn–30 wt% $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC, Gimat) composite electrodes were screen printed on both sides of SDC disks to prepare symmetry cells for electrochemical impedance spectroscopy (EIS). The SDC substrate disks, 10 mm in diameter and 0.5 mm in thickness, were prepared by solid-state sintering at 1600 °C for 4 h. A slurry with proper viscosity for screen printing was typically obtained by ball-milling a mixture of 0.3 g BSLFMn ($x = 0.0$–0.20) with 0.13 g SDC powder and ethyl cellulose–terpineol (J.T. Baker) binder.[14] After screen printing, the cells were baked at 120 °C and then sintered at 1050 °C for 5 h. The EIS was measured using an impedance analyzer (HIOKI, 3532-50) at 30 mV, operating at frequencies ranging from 0.01 Hz to 1 MHz at temperatures ranging from 600–800 °C.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the BSLFMn samples sintered at 1050 °C for 5 h. All the samples were found to have an ABO_3 cubic perovskite type structure. The XRD peaks of all samples fitted well with the standard peaks of $BaFeO_{3-\delta}$ (JCPDS 75-0426). The peaks were found to gradually shift toward the high-angle direction but no other second phases were detected as the amount of Mn-doping increased. The lattice parameter a and unit cell volumes of the BSLFMn samples are shown in Fig. 1(b). The lattice parameter a of $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ decreased from 3.912 Å to 3.895 Å and the cell volume decrease from 59.79 $Å^3$ to 59.09 $Å^3$

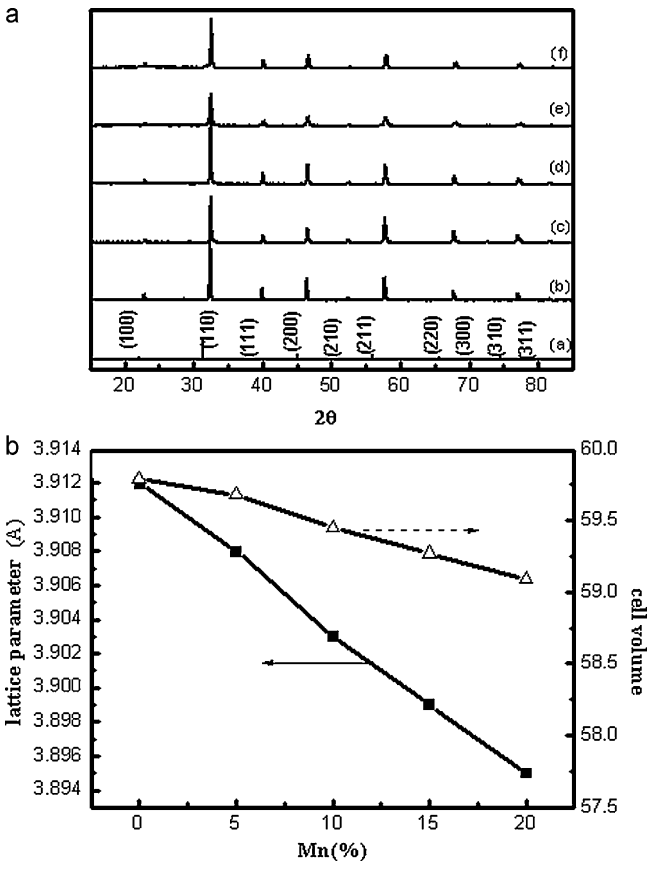

Fig. 1. (A) XRD patterns of $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$. (a) $BaFeO_3$ JCPDF 75-0426, (b) $x = 0.00$, (c) $x = 0.05$, (d) $x = 0.10$, (e) $x = 0.15$ and (f) $x = 0.20$. (B) Lattice parameter and cell volume of $(Ba_{0.5}Sr_{0.5})_{0.8}La_{0.2}Fe_{1-x}Mn_xO_{3-\delta}$ depends on x.