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Evaluation of $La_{0.3}Ca_{0.7}Fe_{1-y}Cr_yO_{3-\delta}$ ($y = 0.1–0.3$) cathodes for intermediate temperature solid oxide fuel cells

Jing Xiao[a], Qing Xu[a,*], Duang-Ping Huang[a], Min Chen[b,*], Kai Zhao[c,1], Bok-Hee Kim[c]

[a] School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, People's Republic of China
[b] Department of Chemistry, University of Oslo, 0349 Oslo, Norway
[c] Division of Advanced Materials Engineering, Hydrogen & Fuel Cell Research Center, Chonbuk National University, Jeonju 561-756, Republic of Korea

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ABSTRACT

Perovskite-type (ABO_3) complex oxides of $La_{0.3}Ca_{0.7}Fe_{1-y}Cr_yO_{3-\delta}$ ($y = 0.1–0.3$) system were prepared via a glycine-nitrate process. In view of utilization as cathode for intermediate temperature solid oxide fuel cells, the structure, electrical conducting, thermal expansion and electrochemical properties of the oxides were investigated in comparison with their strontium counterparts ($La_{0.3}Sr_{0.7}Fe_{1-y}Cr_yO_{3-\delta}$, $y = 0.1–0.3$). Differences in the properties between the two systems were interpreted in relation with their structural characteristics. The results corroborate the effectiveness of modulating A-site dimension in modifying the overall properties of iron chromium-based perovskite-type cathode materials. The calcium compositions with $y = 0.2$ and $y = 0.3$, respectively, exhibit the optimal overall properties, superior to their strontium counterparts. The good overall properties of the two compositions, including suitable thermal expansion coefficients ($11–12 \times 10^{-6}\,K^{-1}$ between 40 and 1000 °C), low polarization resistances (~$0.12\,\Omega\,cm^2$ at 800 °C) and acceptable electrical conductivity (~$40\,S\,cm^{-1}$ at 800 °C), demonstrate their potential in cathode utilization.

1. Introduction

Solid oxide fuel cells (SOFCs) are high efficiency energy conversion devices with attractive merits of environmental compatibility and fuel versatility [1]. In view of the competitiveness of SOFC technology, it is indispensable to reduce the operation temperatures of the devices down to intermediate temperatures (600–800 °C) or even lower. Developing superior SOFC materials, especially electrode and electrolyte materials, plays an important role in paving the way towards this aim.

At intermediate temperatures, oxygen-deficient cobalt-based perovskites, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF), exhibit excellent mixed ionic-electronic conductivity and catalytic activity towards oxygen reduction [2–5]. In the past decades, they have been the representative cathode materials of intermediate temperature SOFCs (IT-SOFCs) [2]. Nevertheless, the thermal expansion coefficients (TECs) of these cobalt-based perovskites are excessively large [4,5]. Meanwhile, their chemical instability under working conditions of a SOFC cathode is unsatisfactory [6,7]. These disadvantages result in a concern on mechanical stability of the SOFC devices utilizing cobalt-based perovskites cathode.

It has been recognized that the TEC and chemical stability problems are related with the inherent peculiarity of the cobalt-based perovskites, i.e. the presence of Co(IV)/Co(III) couples in the structures [8]. Therefore, intensive efforts have been made to explore cobalt-free cathodes for IT-SOFCs [6–12]. Sr^{2+} or Ca^{2+}-doped lanthanum chromite-based perovskites are known as candidate materials for interconnectors of IT-SOFCs [1,13,14]. Moreover, Sr^{2+}-doped lanthanum chromite-based perovskites have been believed to be a promising anode material for IT-SOFCs, due to high redox stability and good catalytic activity for oxidation of fuels (e.g. methane) [15,16]. Interestingly, $La_{0.3}Sr_{0.7}Fe_{1-y}Cr_yO_{3-\delta}$ ($y = 0.1–0.3$, LSFCr), a series of newly-developed Sr^{2+}-rich iron chromium-based perovskites, exhibits a variety of desirable characteristics for utilization as cathodes in IT-SOFCs [17]. These LSFCr perovskites have robust structural stability, high electrical conductivity and superior catalytic ability towards oxygen reduction. Moreover, anode-supported single cells with LSFCr cathodes present a good performance at intermediate temperatures.

A SOFC cathode, as well known, should be thermodynamically compatible with other device components, especially the

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* Corresponding authors.
E-mail addresses: xuqing@whut.edu.cn (Q. Xu), minchen1981@126.com (M. Chen).

[1] Present address: The Voiland School of Chemical Engineering & Bioengineering, Washington State University, PO Box 646515 Pullman, WA 99164-2710, United States.

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electrolyte. Regrettably, the TECs of LSFCr ($16–19 \times 10^{-6}\,K^{-1}$ between 50 and 900 °C) are dissatisfactory with respect to the compatibility demand [17]. Therefore, further effort is needed to modify the overall properties of LSFCr perovskites.

Modulating the A-site dimension of pervoskite-type mixed-conducting cathode materials is viable to tune their structure and thereby properties, with a reduced A-site dimension favoring a lowered TEC [18,19]. Hence, it is expected that replacing the Sr^{2+} in LSFCr with smaller Ca^{2+} might be a solution to the TEC problem of the system. Our previous work on $La_{1-x}Ca_xFe_{0.8}Cr_{0.2}O_{3-\delta}$ (x = 0.5–0.7) compositions has preliminarily validated this expectation [20].

To further examine the effect of A-site modulation, we extended the preliminary attempt to $La_{0.3}Ca_{0.7}Fe_{1-y}Cr_yO_{3-\delta}$ (y = 0.1–0.3, LCFCr) system. In this work, we investigate the structure, electrical conducting, thermal expansion and electrochemical properties of LCFCr compositions in comparison with LSFCr system. Difference in these properties between the two systems was diagnosed in relation with their structures. The overall properties of LCFCr were evaluated from the viewpoint of cathode application in IT-SOFCs.

2. Experimental

2.1. Synthesis and preparation procedures

In this work, all the raw materials were reagent grade chemicals provided by domestic commercial suppliers. These chemicals were used as received without further purification. LCFCr powders were synthesized using a glycine-nitrate process [19,20] and calcined at 950 °C for 2 h.

To inspect the electrical conducting and thermal expansion properties of LCFCr, rectangular bar-shaped ceramic specimens were prepared by the conventional solid state sintering technique [20]. The ceramic specimens were sintered at 1250 °C for 2 h in air.

To examine the electrochemical properties of LCFCr, three-electrode half cells based on $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) electrolyte and with LCFCr as working electrodes were prepared using a screen-printing technique [20]. Configurations and geometrical parameters of the half cells were almost identical to those depicted in our earlier paper [21], except for varied working electrodes.

2.2. Structure analyses

The phase purity of synthesized powders and crystal structure of ceramic specimens were investigated using a Philips X′pert PRO X-ray diffractometer with Cu Kα radiation. The X-ray diffraction (XRD) data of ceramic specimens were analyzed using MDI Jade 6.0 software. The morphology of synthesized powders was checked using a field emission scanning electron microscope (FESEM, Carl Zeiss SUPRA 40VP). The microstructures of ceramic specimens and half cells were observed using a JEOL JSM-5610LV scanning electron microscope (SEM). The observed ceramic specimens were polished and thermally etched. The microstructure parameters of half cells were estimated by image analysis using Image Profession Plus software.

The oxygen non-stoichiometry (δ) of LCFCr was determined by the iodometric titration [22,23] and thermogravimetric (TG) methods [17], respectively. The specimens tested by the iodometric titration method were heated in air at pre-set temperatures for 8 h, followed by quenching in liquid nitrogen. As for the TG measurement, the oxygen content in LCFCr was recorded as a function of temperature using a Netzsch STA 449C thermal analyzer. The measurement was performed in air between 30 and 900 °C upon cooling at a rate of $2\,°C\,min^{-1}$. The δ values at different temperatures were derived from recorded data.

2.3. Property measurements

The density of ceramic specimens was measured by the Archimedes method using ethanol medium. The electrical conductivity was measured using direct current (dc) four-terminal method at 150–900 °C in air. At every measurement temperature, the data of tested specimens were recorded after holding at the temperature for 30 min. The thermal expansion was monitored using a Netzsch DIL 402C dilatometer. The measurement was performed in air between 40 and 1000 °C upon heating at a rate of $10\,°C\,min^{-1}$. An alumina bar was used as the standard to calibrate measured data.

The electrochemical properties of LCFCr electrodes were investigated using a CHI 660C electrochemical work station at 800 °C in air. The electrochemical impedance spectroscopy of the half cells was measured under open circuit conditions in the range of 0. 01 Hz–100 kHz. The amplitude of testing signals was 15 mV. The measured impedance data were deconvoluted using Zview 3.1a program. The cathodic polarization curves of the electrodes were measured using the chronopotentiometry technique [24].

3. Results and discussion

3.1. Structural characteristics

Fig. 1 shows the XRD patterns of calcined powders. A single-phase perovskite structure (JCPDS Card No.89-0481) was certified for the powders with different chromium contents. FESEM observation demonstrated that the particles of the powders are superfine and homogeneous (~120 nm). The inset illustrates typical particle morphology of the powders.

The crystal structure of LCFCr ceramic specimens was analyzed using the Rietveld method. Fig. 2a shows the refined patterns of the specimen with y = 0.3. The calculated profiles agree well with the experimental result, with the *R* factor (residual error of fit) less than 5%. Similar results were obtained for the other two specimens. The Rietveld analysis identified that LCFCr has an orthorhombic structure (*Pnma* space group), different from the rhombohedral structure (*R*-3*c* space group) of LSFCr [17]. This difference is attributed to the smaller ionic radius of Ca^{2+} (1.34 Å in twelve-fold coordination) than Sr^{2+} (1.44 Å in twelve-fold coordination) [25], resulting in varied A-site dimensions and therefore differing structural symmetries for the two perovskite systems. Similar phenomena, i.e. rhombohedral-to-orthorhombic structural change with reducing A-site dimension, have been found for various

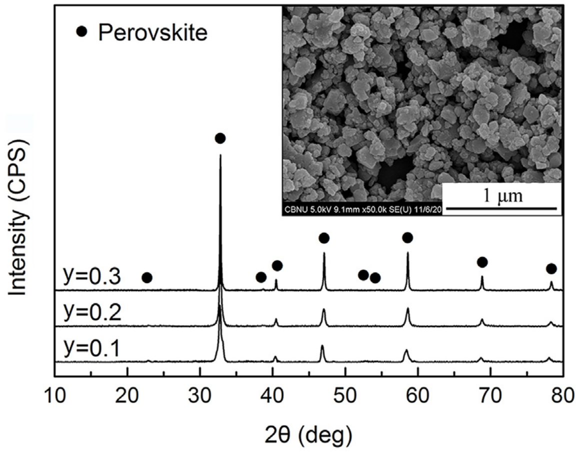

Fig. 1. XRD patterns of calcined LCFCr powders. The inset shows the FESEM image of the powder with y = 0.3.