Solid State Ionics 180 (2009) 973–977

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

A-deficit LSCF for intermediate temperature solid oxide fuel cells

Baoan Fan [a,*], Xiangli Liu [b]

[a] Key Laboratory of Coal Conversion and New Carbon Materials, Hubei Province, Wuhan University of Science and Technology, Wuhan 430081, P.R. China
[b] College of Chemical Engineering, Jiujiang University, Jiujiang Jiangxi 332005, P.R. China

ARTICLE INFO

Article history:
Received 20 May 2008
Received in revised form 17 March 2009
Accepted 26 March 2009

Keywords:
Strontium doped lanthanum cobalt ferrite
Cathode material
Solid oxide fuel cells
Nonstoichiometry

ABSTRACT

A-deficit $La_{0.54}Sr_{0.44}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathode material for intermediate temperature solid oxide fuel cells (IT-SOFCs) was synthesized by a citrate complexation (Pechini) route. Using $La_{0.54}Sr_{0.44}Co_{0.2}Fe_{0.8}O_{3-\delta}$ as cathode material, a superior cell performance with the maximum power density of 309, 470 and 855 mW cm^{-2} at 600, 650 and 700 °C was achieved, in contrast with the maximum power density of 266, 354 and 589 mW cm^{-2} using conventional $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ as cathode material at the same temperatures. The reason of this improvement was analyzed on the basis of defect chemistry. Thermal shrinkage experiment testified that the oxygen vacancies in $La_{0.54}Sr_{0.44}Co_{0.2}Fe_{0.8}O_{3-\delta}$ are more mobile than in $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$. Furthermore, theoretical calculation in terms of their composition and the shift of peak position in XRD pattern showed that the concentration of oxygen vacancies of $La_{0.54}Sr_{0.44}Co_{0.2}Fe_{0.8}O_{3-\delta}$ is higher than that of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$. Therefore, the oxygen ion conductivity via vacancies transfer mechanism is enhanced, which induces the polarization resistance of $La_{0.54}Sr_{0.44}Co_{0.2}Fe_{0.8}O_{3-\delta}$ being decreased with a result of cell performance improved.

1. Introduction

Solid oxide fuel cells (SOFCs) offer a low-pollution technology to generate electricity electrochemically with high efficiency. Current efforts aim at decreasing the cost of SOFC by lowering cell operation temperature to 700 °C or less [1,2]. One of the critical challenges for operating SOFCs at low temperature is how to reduce polarization losses of electrodes [3]. Many studies have showed that the cathode polarization was the major contribution to the total polarization losses in SOFCs [4]. Therefore reducing cathode polarization resistance is crucial to achieve a desirable cell performance at intermediate temperature range (600–800 °C). Compared with conventional state-of-the-art LSM ($La_{1-x}Sr_xMnO_{3-\delta}$) cathode material, the perovskite-type LSCF ($La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$) provides a more potential candidate for its mixed ionic and electronic conductive ability [5]. Generally, its electronic and ionic conductivities and catalytic activity are enhanced with increase of x and decrease of y, whereas there is an opposite tendency for its chemical compatibility and TEC (Thermal Expansion Coefficient) match with electrolyte [6]. The optimal compromise between above two category properties was found in the composition of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF-6428) [7].

Although the electronic conductivity of LSCF-6428 is high enough (about 300 S cm^{-1} at 750 °C [8]), its oxygen ion conductivity via oxygen vacancies transfer is rather low (about 1×10^{-3} S cm^{-1} at 750 °C [9]). One way to enhance its oxygen ion conductivity is extrinsically adding oxygen ion conductor, such as GDC ($Ce_{1-x}Gd_xO_{2-\delta}$), to LSCF. Dusastre et al. found that the cathode polarization resistance decreased four times when 36 vol.% $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ was mixed with LSCF [10]. Murray et al. also found that addition of 50 vol.% $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ to LSCF resulted in a factor of about 10 decreases in the polarization resistance [11]. However, the sinter ability and TEC of LSCF and GDC must be matched carefully, or else the composite cathode would be delaminated. Another way to overcome the obstacle is to tailor the composition of LSCF via an A-deficit strategy to increase the LSCF oxygen ion conductivity intrinsically by creating more oxygen vacancies. Mai et al. demonstrated that $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ showed a high power density (about 1.0 W cm^{-2} at 750 °C) in contrast with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (about 0.56 W cm^{-2} at 750 °C) at the same conditions [12]. Doshi et al. also reported that using $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$ as cathode material the cell initial electrode resistance was only 0.1 $\Omega\cdot cm^2$ at 500 °C [13]. However, its defect chemistry as well as the mechanism giving such low electrode resistance for A-deficit LSCF has not been discussed yet.

In this paper, an optimized A-deficit LSCF with the composition of $La_{0.54}Sr_{0.44}Co_{0.2}Fe_{0.8}O_{3-\delta}$ was synthesized by a Pechini method where citric acid is used as complexant and fuel. In addition, the relationship between oxygen nonstoichiometry of LSCF and electrochemical polarization behavior was discussed based on defect chemistry.

2. Experimental

2.1. Powder synthesis

The LSCF powder was synthesized by a citrate complexation (Pechini) route. The analytical reagent of lanthanum oxide (La_2O_3), strontium

---

[*] Corresponding author. Mail box: 144, Wuhan University of Science and Technology, Wuhan, China 430081. Tel.: +8613297099152; fax: +86-027-86568662
E-mail address: fanbaoan@yahoo.com.cn (B. Fan).

0167-2738/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.ssi.2009.03.017

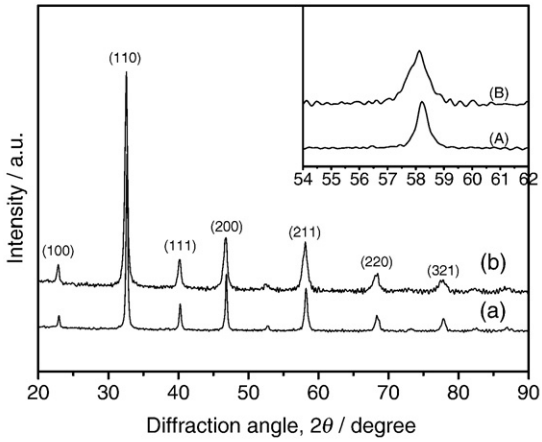

Fig. 1. XRD patterns of (a) LSCF-60/40 and (b) LSCF-54/44.

carbonate ($SrCO_3$), cobaltous nitrate ($Co(NO_3)_2 \cdot 6H_2O$) and ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were precisely weighed at the composition and the mass of LSCF desired to be synthesized. First, the La_2O_3 was dispersed in little deioned water and dissolved by adding concentrated nitric acid (HNO_3, 65.0–68.0 wt.%) dropwise under stirring. Secondly, the $SrCO_3$ was also dissolved by adding concentrated nitric acid drop by drop so that there is no extra nitric acid remainder. Next, the $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in the solution followed by adding citric acid at the molar percentage of 1.5 to all metal ions. Then, the pH value of the solution was adjusted to about 8 by dropping concentrated ammonia solution (25.0–28.0 wt.%). Subsequently, the solution was heated to evaporate water until it turned to a viscous sol, which was placed in a Muffle oven afterwards and fired at 400 °C for 30 min to burn out organic ingredients. After cooling down to room temperature, the precursor foam was collected for subsequent bake at 700 °C for 5 h with a heating rate of 10 °C min^{-1}.

2.2. Cell fabrication

Black nickel oxide powder (NiO, HSG-010-1998, Biyan, Beijing China) and nano-sized 8YSZ powder ($[Y_2O_3]_{0.08}[ZrO_2]_{0.92}$, HWY-N-13.5, Huawang, Guangdong China, $D_{50} = 153$ nm) was used to prepare Ni-8YSZ ceramic anode substrates. The powder was mixed in a composition of 65 wt.% NiO and 35 wt.% 8YSZ by ball milling at 600 rpm for 12 h with ethanol as dispersant. After the ethanol has been evaporated completely, the anode powder was crushed and then compacted under uniaxial pressure of 62 MPa to form a disc with a diameter about 20 mm and a thickness about 1 mm. The green anode disc was subsequently calcined at 800 °C for 2 h to strengthen the mechanical property of the anode substrates. A thin film of 8YSZ electrolyte layer was deposited on the one side of anode substrates by a dip-coating technique. Next, the anode and 8YSZ electrolyte bi-layer was sintered at 1250 °C for 2 h to achieve a dense electrolyte film with a thickness of about 8 μm. After being sintered, the thickness of the anode substrates was about 0.8 mm and the diameter of the bi-layer was about 16 mm.

Table 1
Crystallographic parameters of LSCF-60/40 and LSCF-54/44.

Crystal cell parameters	*a* (Å)	*b* (Å)	*c* (Å)	*V* ($Å^3$)	Calculated density [a] ($g\ cm^{-3}$)	XRD density[b] ($g\ cm^{-3}$)
LSCF-60/40	3.8753	3.8769	3.8827	58.3343	6.34	6.36
LSCF-54/44	3.8866	3.8793	3.8837	58.5557	6.18	

[a] From XRD analysis of as-calcined powder.
[b] From literature reported by Tai et al. [16].

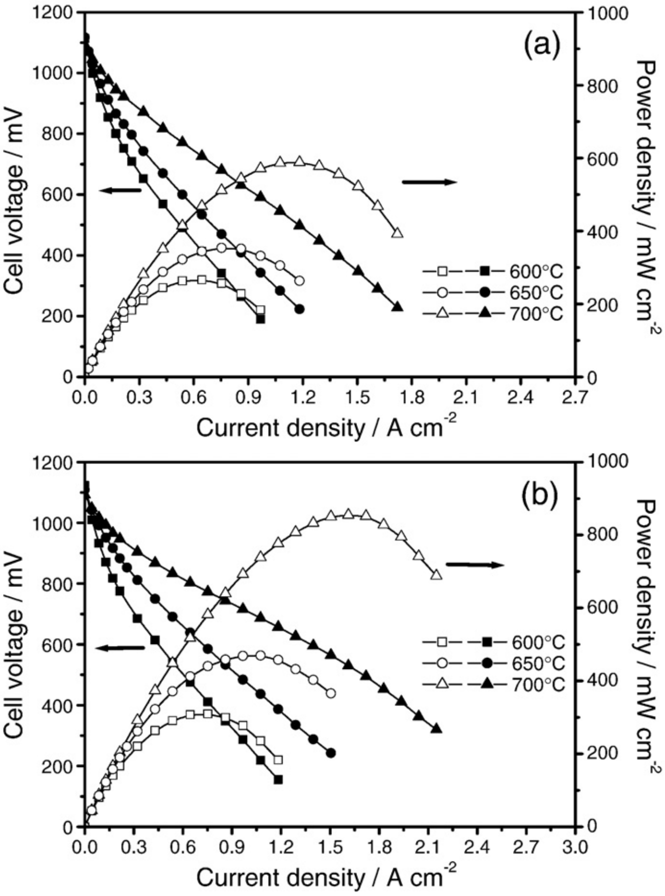

Fig. 2. Cells performance with (a) LSCF-60/40 and (b) LSCF-54/44 as cathode.

The cathode paste was prepared by ball milling the LSCF powder with terpineol at a solid content of 25% at 800 rpm for 30 h, to which 0.5% ethyl cellulose (EC) as film-forming reagent and 5% additif mouillant et (disperbyk-2050, BYK chemie, Germany) as dispersant were added relative to the LSCF powder. The paste was subsequently applied on the electrolyte side of the bi-layer using a screen-printing technique to form a complete cell, which followed by sintered at 800 °C for 2 h. The thickness of LSCF cathode was about 6 μm and the cathode area was 0.465 cm^2.

2.3. Cell test

Cells performance was performed using a home-made measurement device. The anode chamber was fed in pure hydrogen, while the cathode was exposed to ambient atmosphere. The anode side was sealed by Ag paste and the cathode surface was brushed with Pt paste as current collector. Two Ag silks were connected to anode and cathode respectively, serving as voltage and current probes. The current–voltage (*I*–*V*) characteristic curves of cells were plotted by measuring closed circuit voltage under constant current density provided by a potentiostat (DJS-292, Leizi Xinjing, Shanghai, China). The cell power density was calculated by the product of closed circuit voltage with current density. AC impedance spectra were measured by an

Table 2
Total resistance of the cells derived from the *I*–*V* curves at the current approaching to zero.

Temperature/°C	600	650	700
R(Cell-1)/Ω cm^2	3.198	1.987	1.116
R(Cell-2)/Ω cm^2	2.627	1.558	0.825