Sensors and Actuators B 230 (2016) 592–599

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

The influence of nonstoichiometry on electrical transport and ethanol sensing characteristics for nanocrystalline $LaFe_xO_{3-\delta}$ sensors

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ARTICLE INFO

Article history:
Received 3 September 2015
Received in revised form 7 February 2016
Accepted 19 February 2016
Available online 26 February 2016

Keywords:
Nonstoichiometry
$LaFeO_3$
XPS
Sensing mechanism
Gas sensor

ABSTRACT

Nonstoichiometric nanocrystalline $LaFe_xO_{3-\delta}$ ($x = 0.7/0.8/0.9/1.0/1.1/1.2/1.3$) powers were prepared by sol–gel method with citric acid. Temperature dependence of resistance for $LaFe_xO_{3-\delta}$ sensors fits best to Holsteins model of small polaron hopping conduction. The resistance is determined by the competition between electrical valence compensation and oxygen vacancy compensation. And at each fixed temperature, the resistance is decreased with the introduction of more Fe deficiency. XPS analysis on O1s and C1s spectra verifies the existence of La-carbonate on the surface. The variation of surface concentration of adsorbed oxygen and La-carbonate, atomic ratio of Fe^{4+}/Fe^{3+} and Fe/La with x value are discussed in combination, which indicate that the release of electrons trapped by native active oxygen due to the decomposition of monodentate La-carbonate also makes contribution to the response of $LaFe_xO_{3-\delta}$ sensors to ethanol, in addition to the major contribution from adsorbed oxygen species. The best sensing performance of nanocrystalline $LaFe_{0.8}O_{3-\delta}$ sensor is ascribed to its relatively large surface concentration of adsorbed oxygen species and monodantate La-carbonate.

1. Introduction

Gas sensors based on $LaFeO_3$ nanoparticles have attracted considerable interests due to their high sensitivity and stability to ethanol and tunable selectivity to various gas by the substitution of cation ions [1–16]. Among various methods that can be used to prepare $LaFeO_3$ nanoparticles, sol–gel method using citric acid has been frequently adopted due to the low cost of raw materials and easy handle of procedures. However, the high resistance of the obtained nanoparticles limits the practical application.

For $LaFeO_3$, its charge carriers are holes produced by the ionization of the La^{3+} cation vacancy defect [17,18]. In order to keep charge neutrality, the substitution of trivalent La or Fe ions by bivalent cation element would lead to the increase of hole concentration by electric valence compensation or decrease of hole concentration by oxygen vacancy compensation. Mangy groups have reported that the partial substitution of La or Fe by lower valent cation elements such as Pb, Mg, Ba, Co, Sr and Ca could reduce the resistance of $LaFeO_3$-based sensors [1–3,5–11,16] by the competition of electric valence and oxygen vacancy compensation. Moreover, the sensing performance to ethanol has also been improved, which is often ascribed to smaller crystallite size and larger amount of adsorbed oxygen species (O_2^- or O^-) [5,10].

It is well known that the sensing properties of nanocrystalline $LaFeO_3$-based sensors are greatly related to oxygen adsorption [1,10]. The oxygen molecules adsorbed on the surfaces of nanograins could capture electrons from $LaFeO_3$, and results in the decrease of resistance of p-type $LaFeO_3$ [19]. However, the surface of lanthanum oxide samples prepared with citric acid would be enriched with carbonate species due to the reaction of CO_2 produced by the combustion process with the lanthanum oxide surface [20–24], therefore, the existence of surface carbonate species which has been neglected should also be considered when exploring the gas sensing mechanism of $LaFeO_3$-based sensors.

In addition to the common means of substitution of cation ions, we speculate that the introduction of intrinsic cation deficiency could be an alternative way to reduce the electrical resistance of perovskite oxides, and thus affect the sensing performance. Therefore, in the present work, we systematically investigated the influence of nonstoichiometry on the electrical transport and ethanol sensing properties of nanocrystalline $LaFe_xO_{3-\delta}$ powders which were prepared by sol–gel method with citric acid, and propose a combined ethanol sensing mechanism by the analysis of

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http://dx.doi.org/10.1016/j.snb.2016.02.096
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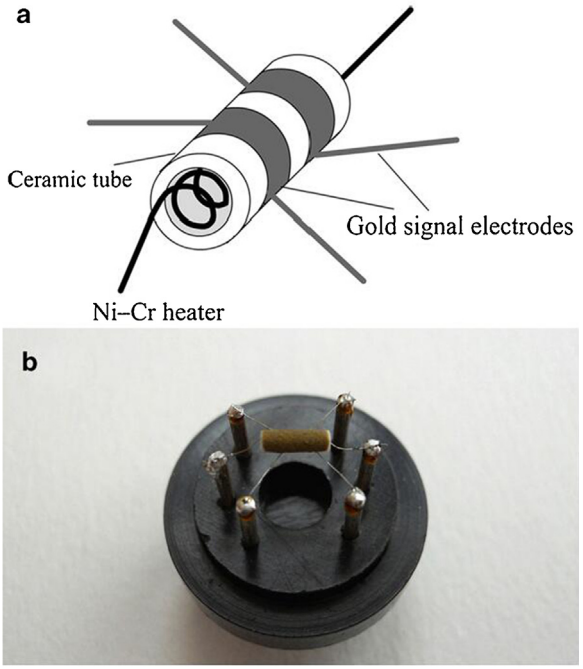

Fig. 1. (a) Schematic image of the sensor structure and (b) a photograph of the sensor.

XPS results, with the consideration of both oxygen adsorption and carbonate formation at the surface region.

2. Experimental

2.1. Preparation of powders

$LaFe_xO_{3-\delta}$ (x = 0.7/0.8/0.9/1.0/1.1/1.2/1.3) powders were prepared by a sol–gel method. Firstly, appropriate amount of $La(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and citric acid (all analytically pure) were dissolved in ion-free water at 80 °C. The polyethylene glycol (PEG) was added into the mixed solution under stirring at 80 °C to obtain the sol and the sol was dried to form gel. Then, gel pieces were formed through combustion process, and were ground to form fine powders. Finally, the fine powders were annealed at 600 °C for 2 h in an oven.

2.2. Characteristics of powders

X-ray diffraction patterns of the obtained $LaFe_xO_{3-\delta}$ powders were measured by X-ray diffractometer (D/max 2500, Rigaku Corporation, Japan) using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements for $LaFe_xO_{3-\delta}$ nanocrystalline powders were performed with monochromated Al Kα radiation using X-ray photoelectron spectrometer (ESCALAB 250, Thermo Electron Corporation, USA).

2.3. Fabrication and measurements of sensors

0.1 g powders obtained above were mixed with 0.1 ml terpineol to form a paste. The sensors were made by coating ceramic tube (outside diameter = 1.2 mm, length = 4 mm) with the paste to form a thin sensing film, then annealed at 600 °C for 2 h in an oven to increase stability. A pair of gold electrodes was installed at each end of the ceramic tube before it was coated with the paste; each electrode was connected with two Pt wires. A Ni–Cr heating wire (diameter = 0.5 mm, resistance = 35 Ω) was inserted into the tube to form an indirect-heated gas sensor. Fig. 1(a) and (b) show the schematic image of the sensor structure and a photograph of the sensor, respectively. The electrical properties of the sensor were measured by an Intelligent Gas Sensing Analysis System (CGS-8, Beijing Elite Tech Co., Ltd., China). The sensor sensitivity was defined as the ratio (S = Rg/Ra) of the resistance of the sensor in target gases (Rg) and that in dry air (Ra). The operating temperature of the sensor was varied between 130 and 200 °C. The response and recovery time were defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of adsorption and desorption, respectively.

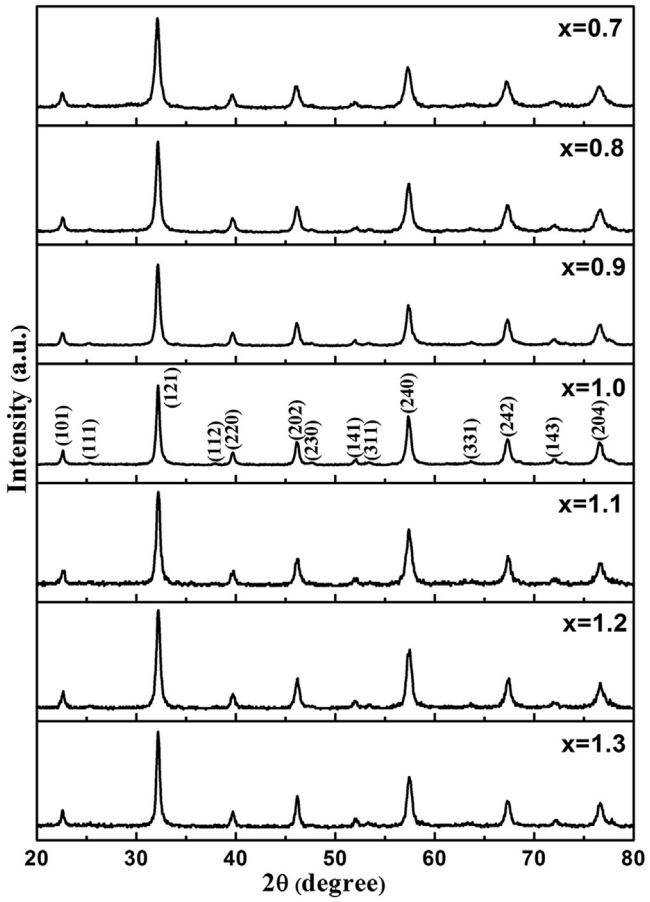

Fig. 2. X-ray diffraction patterns of $LaFe_xO_{3-\delta}$ powers annealed at 600 °C with different x value.

3. Results and discussion

3.1. Structural analysis

Fig. 2 shows the X-ray diffraction patterns of $LaFe_xO_{3-\delta}$ powers annealed at 600 °C with different x value. All the samples have a single phase with orthorhombic perovskite structure (space group Pnma-62), without any trace of impurity phase. Their lattice parameters, unit cell volumes, and average crystallite sizes are summarized in Table 1. The lattice parameters were calculated from peak positions and miller indices using Bragg law $2d\sin\theta = n\lambda$ and $1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$, where d is the interplanar spacing, h k and l are miller indices, a b and c are lattice parameters. Each lattice parameter changes with x values in its own way. The unit cell volume is calculated by the product of a b and c. Compared to the sample with x = 1.0, the unit cell volumes for the sample with x < 1.0 are larger, while the ones for the sample with x > 1.0 are smaller, indicating that the introduction of Fe deficiency results in the expansion of unit cell, while the introduction of La defi-