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Sintering, microstructure and conductivity of $La_2NiO_{4+\delta}$ ceramic

Duan-Ping Huang, Qing Xu *, Wen Chen, Feng Zhang, Han-Xing Liu

School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, People's Republic of China

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Abstract

Microstructure and electrical conducting properties of $La_2NiO_{4+\delta}$ ceramic were investigated in the sintering temperature range 1200–1400 °C. The results demonstrate that the microstructure and electrical conducting properties of $La_2NiO_{4+\delta}$ ceramic are sensitive to sintering temperature. Compared with a progressive densification development with sintering temperature from 1200 to 1300 °C along with an insignificant change in grain size, there is an exaggerated grain growth in the specimens sintered at higher temperatures. Increasing sintering temperature from 1200 to 1300 °C resulted in an enhancement of electrical conducting properties. Further increase of sintering temperature exceeding 1300 °C reduced the electrical conducting properties. A close relation between the microstructure and electrical conducting properties was suggested for $La_2NiO_{4+\delta}$ ceramic. With respect to the electrical conducting properties, the preferred sintering temperature of $La_2NiO_{4+\delta}$ ceramic was ascertained to be 1300 °C. The specimen sintered at 1300 °C exhibits a generally uniform microstructure together with electrical conductivities of 76–95 S cm^{-1} at 600–800 °C.

Keywords: A. Sintering; C. Electrical properties; Microstructure; $La_2NiO_{4+\delta}$

1. Introduction

Mixed electronic-ionic conductors are of great research interest because of their various potential applications, such as cathodes for intermediate temperature (600–800 °C) solid oxide fuel cells (SOFCs), oxygen separation membranes, membrane reactors for syngas production and catalysts for oxidation of hydrocarbons [1–4]. It has been well established that using the mixed conductors as cathodes for intermediate temperature SOFCs results in an increase of the triple phase boundary (TPB) length and a decrease of cathodic polarization [2,4]. In the past two decades, much work on the cathode materials for intermediate temperature SOFCs focused on oxygen-deficient perovskite-type oxides such as $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ (LSFC). However, the LSFC materials suffer from excessively large thermal expansion coefficients, making it difficult in matching with other components of intermediate temperature SOFCs, such as solid state electrolyte [5,6]. Recently, oxygen hyperstoichiometric $La_2NiO_{4+\delta}$ based compounds with a K_2NiF_4 structure have attracted growing attention as a novel mixed conductor [6–12]. These materials exhibit high oxygen diffusion and surface exchange coefficients at intermediate temperatures together with moderate thermal expansion coefficients around 13.0×10^{-6} K^{-1} [13,14]. These desired properties make them promising candidate materials as cathodes for intermediate temperature SOFCs.

Microstructure is an important contributing factor to the transport properties of mixed conducting materials [15]. As well known, the microstructure of ceramic materials, to a great extent, relies on sintering conditions. Thus, the influence of sintering temperature on the microstructure and electrical conducting properties of $La_2NiO_{4+\delta}$ is an intriguing subject of significant importance. Up to date, the research on this topic is comparatively limited. In this work, the microstructure and electrical conducting properties of $La_2NiO_{4+\delta}$ ceramic were investigated in the sintering temperature interval 1200–1400 °C. Moreover, the microstructural dependence of the electrical properties has also been examined.

2. Experimental

Reagent grade lanthanum hydroxide ($La(OH)_3$), nickel carbonate ($NiCO_3{\cdot}2Ni(OH)_2{\cdot}4H_2O$) and diethylenetriamine-pentaacetic acid (H_5DTPA) were used as starting materials.

* Corresponding author. Tel.: +86 27 87863277; fax: +86 27 87864580.
E-mail address: xuqing@whut.edu.cn (Q. Xu).

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$La_2NiO_{4+\delta}$ powder was synthesized by a polyaminocarboxylate complex method. A designed amount of H_5DTPA was mixed with lanthanum hydroxide and nickel carbonate in deionized water. The mixture was stirred at 90 °C to form a blue and transparent aqueous solution, then heated in an oven at 100 °C to yield a solid polyaminocarboxylate complex. The solid complex precursor was pulverized and calcined at 900 °C for 2 h in air. The detail of the synthesis process has been reported elsewhere [16]. A pure K_2NiF_4 phase was identified for the resulting powder by X-ray diffraction (XRD). Scanning electron microscopy (SEM) analysis shows that the powder consists of homogeneous and fine particles of 100–200 nm in size. The powder was uniaxially pressed into rectangular bars (30 mm × 4 mm × 4 mm) and disks (13 mm diameter and 2 mm thickness) under a pressure of 300 MPa, respectively. Then, the compacted powders were sintered at 1200–1400 °C for 4 h in air.

The crystal structure of the ceramic specimens was examined by a X'Pert PRO X-ray diffractometry using Cu Kα radiation. The XRD data were collected over a 2θ range from 20° to 100° in a step of 0.02°. Diffraction data were analyzed by the Rietveld method using the FULLPROF program [17]. The oxygen nonstoichiometry (δ) of the ceramic specimens at room temperature was determined by the iodometry titration method as described in a previous literature [2]. The microstructure of the ceramic specimens was investigated at a Jeol JSM-5610LV SEM using thermally etched polished surfaces. The density of the ceramic specimens was measured by the Archimedes method using pure ethanol. The relative density was derived from the measured density and theoretical density determined by the Rietiveld method using XRD data. The rectangular specimens were polished to ensure surface flatness and painted with platinum paste for measuring electrical conductivity. The electrical conductivity was measured at 50–900 °C by a dc four-terminal method in air.

3. Results and discussion

The XRD pattern of $La_2NiO_{4+\delta}$ sintered at 1300 °C can be indexed in an orthorhombic symmetry with space group Fmmm. The Rietveld refinement profiles of the specimen sintered at 1300 °C are shown in Fig. 1. The profile R-value (R_p), weighted-profile R-value (R_{wp}) and χ^2-value of the refined structure parameters are 8.1%, 10.1% and 3.02%, respectively, indicating that the refinement results are acceptable. The refined lattice parameters of $a = 5.4612(6)$ Å, $b = 5.4584(0)$ Å and $c = 12.6714(9)$ Å are basically consistent with the results of the previous researches [4,18]. The Rietveld refinement was also performed for the specimens sintered at other temperatures, indicating an orthorhombic symmetry for these specimens and rather similar refined lattice parameters to those of the specimen sintered at 1300 °C. The iodometry titration result revealed slightly changed oxygen nonstoichiometry (δ) values of 0.13–0.15 for $La_2NiO_{4+\delta}$ ceramics sintered at different temperatures. Considering the uncertainty of the iodometry titration method (±0.01) [2], the influence of sintering temperature on the oxygen nonstoichiometry of the ceramic can be regarded as almost negligible. Therefore, no remarkable influence of sintering temperature on the crystal structure of $La_2NiO_{4+\delta}$ ceramic was detected.

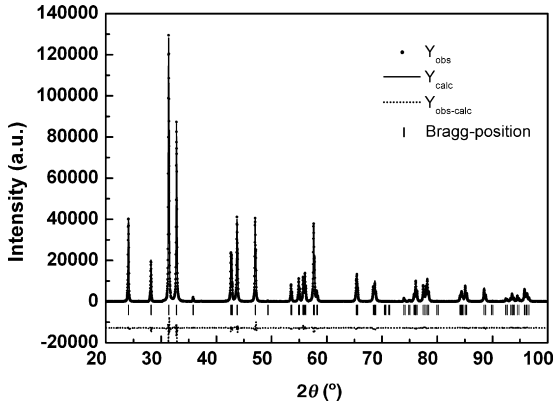

Fig. 1. Rietveld refinement profiles of $La_2NiO_{4+\delta}$ ceramic sintered at 1300 °C (space group *Fmmm*). The observed data are indicated by dots and the calculated data by the solid line overlaying them. The short vertical lines mark the positions of possible Bragg reflections, and the broken line shows the difference between the observed and calculated powder diffraction patterns.

Fig. 2 shows the linear shrinkage and relative density of $La_2NiO_{4+\delta}$ ceramic as a function of sintering temperature. A monotonous increase in linear shrinkage and relatively density with sintering temperature from 1200 to 1400 °C can be observed, which enhance from 9.4 to 13.8% and 86.4 to 95.6%, respectively. Fig. 3 shows the SEM micrographs of $La_2NiO_{4+\delta}$ ceramics sintered at different temperatures. In general, the increase of sintering temperature promoted grain growth and microstructural densification. This is in agreement with the linear shrinkage and relative density data. In the sintering temperature range of 1200–1300 °C, one can see a progressive densification development with increasing sintering temperature in addition to an insignificant change in grain size. A generally uniform microstructure composed of well grown grains around 1 μm was achieved at the sintering temperature of 1300 °C. The specimen sintering at this temperature attains 93.3% of the theoretical density. By comparison, there is a facilitated grain growth in the specimens sintered at higher temperatures, with the grain size remarkably increasing to

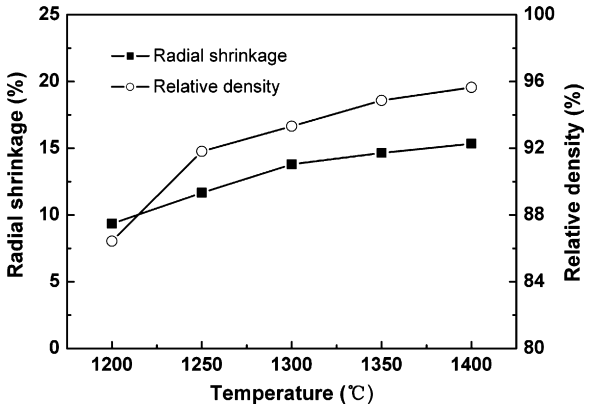

Fig. 2. Linear shrinkage and relative density of $La_2NiO_{4+\delta}$ ceramic as a function of sintering temperature.

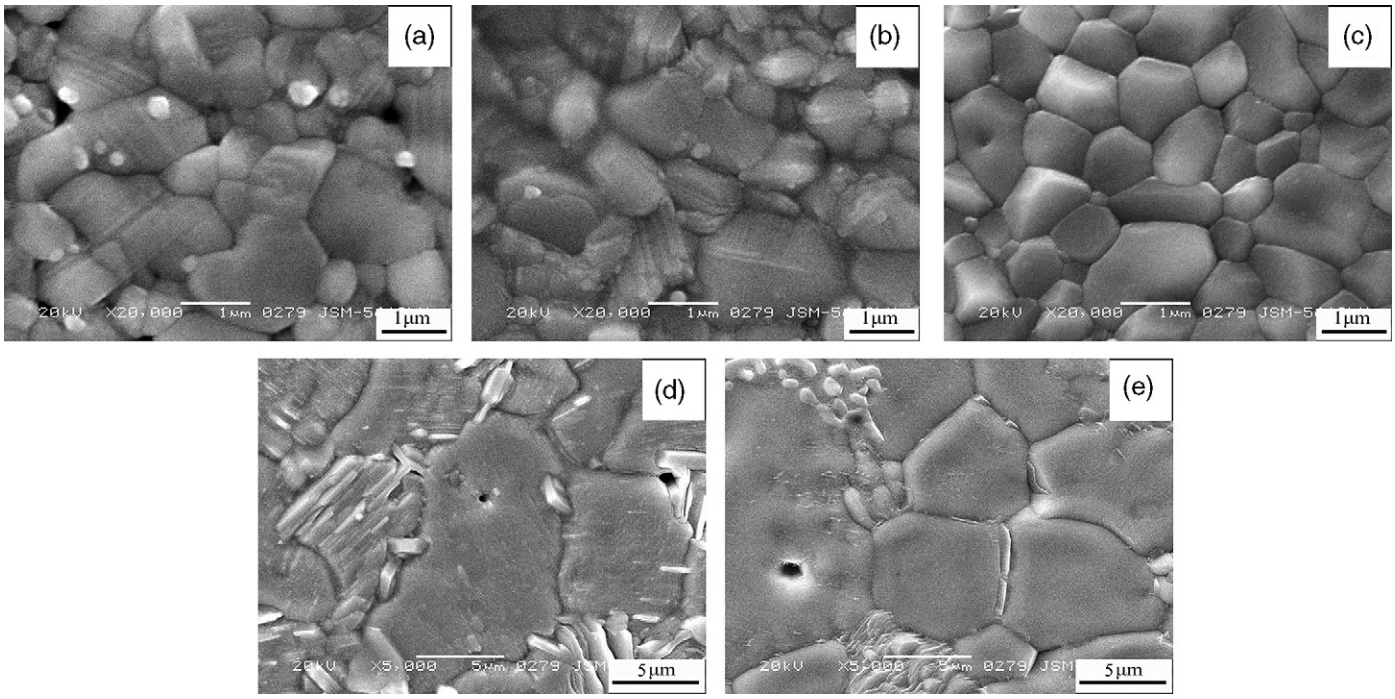

Fig. 3. SEM micrographs of $La_2NiO_{4+\delta}$ ceramics sintered at (a) 1200 °C, (b) 1250 °C, (c) 1300 °C, (d) 1350 °C and (e) 1400 °C.

about 5 μm and several abnormally grown grains appearing. This occurrence implies a considerable increase in the amount of liquid phase above the sintering temperature of 1300 °C. These results refer to significant sintering temperature dependence for the microstructure of $La_2NiO_{4+\delta}$ ceramic. One can note that excessively increasing sintering temperature is prone to cause a deterioration of microstructural uniformity in spite of increased densification.

Fig. 4 shows the electrical conductivity (denoted as σ) of $La_2NiO_{4+\delta}$ ceramic as a function of measuring temperature. Due to the low oxygen ionic transport number of $La_2NiO_{4+\delta}$ based compounds (generally 10^{-4} to 10^{-2}), the electrical conductivity measured by the dc four-terminal method can be regarded as the representative of electronic conductivity [3]. The electrical conductivities of the specimens sintered at different temperatures display an identical variation with measuring temperature, increasing with measuring temperature up to a maximum value near 450 °C and then decreasing. Such a transition in electrical conduction from semiconducting to metallic behavior is similar to previous reported results [12,19]. In the case of a same measuring temperature, the electrical conductivity increases with sintering temperature and attains the largest value at 1300 °C, followed by a decrease of electrical conductivity with further elevated sintering temperature. The specimen sintered at 1300 °C offers a maximum electrical conductivity of 103 S cm^{-1}, which is comparatively larger than literature data of ~80 S cm^{-1} and ~90 S cm^{-1} obtained from the specimens made by the solid state reaction method [10,19] and citrate gel method [8], respectively. At intermediated temperatures (600–800 °C), the specimen gives electrical conductivities of 76–95 S cm^{-1}, roughly near to the least conductivity requirement for cathode materials of SOFCs.

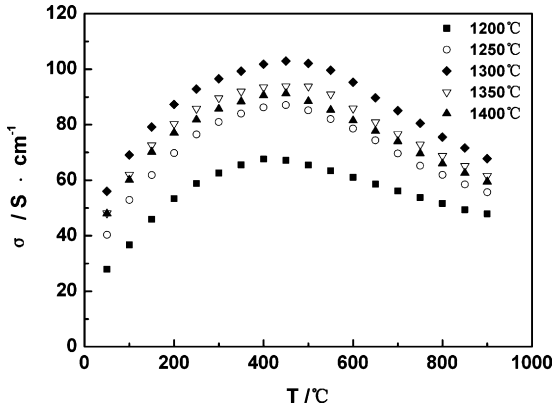

Fig. 4. Temperature dependence of electrical conductivity (σ) for $La_2NiO_{4+\delta}$ ceramics sintered at different temperatures.

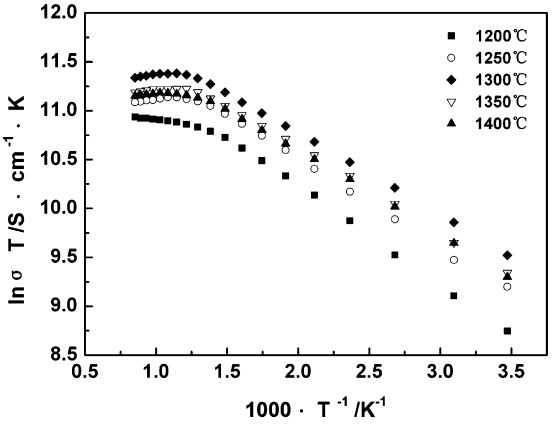

Fig. 5. Plots of ln σT vs. 1000/T for $La_2NiO_{4+\delta}$ ceramics sintered at different temperatures.

Fig. 5 shows the plots of ln σT versus 1000/T for $La_2NiO_{4+\delta}$ ceramics sintered at different temperatures. The plots are nearly linear at low temperatures, suggesting that small polaron hopping is the predominant mechanism for the electrical conduction [3]. At higher temperatures, the plots present a negative deviation from linearity. It is attributed to an extensive loss of hyperstoichiometric oxygen, decreasing the concentration of electronic carrier [13]. The values of activation energy for small polaron hopping (E_a) were calculated from the linear fit of the Arrhenius plots in Fig. 5 over low temperature ranges. Fig. 6 shows the E_a of $La_2NiO_{4+\delta}$ ceramic as a function of sintering temperature. It can be found that the E_a declines with increasing sintering temperature through a minimum value at 1300 °C and then slightly increases.

As well established, the electrical conduction of $La_2NiO_{4+\delta}$ ceramic is essentially a kind of bulk transport [13]. The conductivity data in the present work indicate an obvious sensitivity of the electrical conducting properties to sintering temperature for $La_2NiO_{4+\delta}$ ceramic. This phenomenon can be qualitatively interpreted with respect to the microstructural evolution with sintering temperature. The enhancement of electrical conducting properties with sintering temperature from 1200 to 1300 °C is reasonably ascribed to the densification development of the ceramic. At higher sintering temperatures, the facilitated grain growth infers to a considerable increase of liquid phase amount. This resulted in a complicated effect on the microstructure and consequently electrical conductivity. On one hand, the increase of the liquid phase can improve mass transport during sintering, favoring grain growth and microstructural densification. This acts as a positive effect on the electrical conduction. On the other hand, the amorphous phase formed by the liquid can be regarded as a kind of heterogeneous component in ceramic bulk from microstructural viewpoint. Thus, the increase of the amorphous serves to block the transport of electrical carriers. The electrical conducting properties of the specimens sintered at temperature exceeding 1300 °C rely on the dual contribution of these two distinct effects. The later effect is likely to be dominant with regard to the conductivity results of the present work. Therefore, a close relation between the microstructure and electrical conducting properties can be suggested. One can conclude that it is crucial to adequately control the sintering temperature of $La_2NiO_{4+\delta}$ ceramic in order to achieve desired microstructure and optimum electrical conducting properties. In terms of the electrical conducting properties, sintering at 1300 °C is ascertained to be preferred for $La_2NiO_{4+\delta}$ ceramic, producing a generally uniform microstructure.

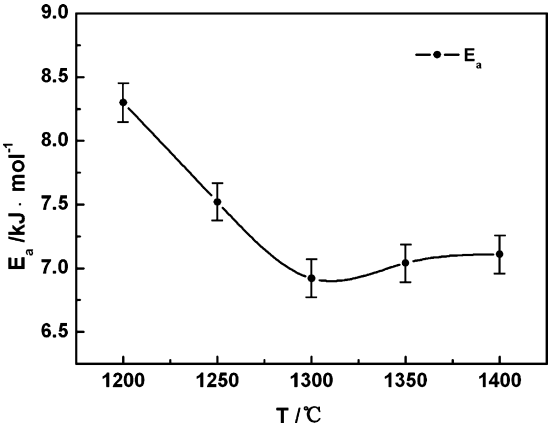

Fig. 6. Activation energy for small polaron hopping (E_a) of $La_2NiO_{4+\delta}$ ceramic as a function of sintering temperature.

4. Conclusions

The microstructure and electrical conducting properties of $La_2NiO_{4+\delta}$ ceramics have been investigated in the sintering temperature range of 1200–1400 °C. It has been determined that the microstructure evolution is responsible for the variation in the electrical conducting properties with sintering temperature. It is important to adequately control the sintering temperature to obtain desired microstructure and optimum electrical conducting properties. The preferred sintering temperature of $La_2NiO_{4+\delta}$ was ascertained to be 1300 °C with regard to the electrical conducting properties. $La_2NiO_{4+\delta}$ ceramic sintered at 1300 °C presents a generally uniform microstructure together with electrical conductivities of 76–95 S cm^{-1} at 600–800 °C.

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