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Synthesis of La_2NiO_4 via a PVA-based route

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Abstract

Single-phase La_2NiO_4 has been prepared using polyvinyl alcohol (PVA) as a complexing agent. Thermogravimetric (TG), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) were used to characterize precursor and derived oxide powders. The particle size and morphologies of La_2NiO_4 crystallites were characterized by field emission scanning electron microscope (FSEM). The effect of the mol ratios of metal ion to hydroxyl groups in polyvinyl alcohol on the formation of La_2NiO_4 was investigated. XRD analysis showed that single-phase and well-crystallized La_2NiO_4 was obtained from precursor with M/OH = 1:3 at 900 °C. The La_2NiO_4 ceramics sintered at 1300 °C for 4 h exhibits an electrical conductivity of 42.5 Ω^{-1} cm^{-1} at room temperature.

Keywords: Sol–gel; Polyvinyl alcohol; La_2NiO_4

1. Introduction

As one of the most promising groups of mixed conductors, oxides with a perovskite-type structure have been widely studied. However, it is still necessary to improve the oxygen permeability and stabilities of these materials to meet the needs of the industrial applications. This has led to an increasing interest in optimizing known materials and developing new MIEC (mixed ionic–electronic conductors) oxides. Recently, La_2NiO_4-based oxides, which originate from the materials with a K_2NiF_4-type structure, have attracted considerable attention, because of the promising oxygen permeability and stabilities [1–7]. La_2NiO_4 based compounds are usually synthesized by the traditional solid state reaction method, but it is difficult to produce pure La_2NiO_4, for which relatively high calcining temperatures (1000–1250 °C), long annealing time (15–30 h) and several intermediate grindings are always needed [8]. A variety of wet chemical methods were also used to synthesize La_2NiO_4. Huang et al. synthesized La_2NiO_4 from diethylenetriaminepentaacetic acid precursor and pure La_2NiO_4 phase was obtained at 900 °C [9]. Fontaine et al. reported a polymeric route based on Pechini's work to synthesize La_2NiO_4 at 1000 °C [10,11]. Guo et al. have prepared phase-pure La_2NiO_4 powders using Pechini method at 1100 °C [12]. Dong et al. successfully prepared La_2NiO_4 samples via the combustion of mixtures with the desired metal ions as cation precursors and glycine as fuel at 1150 °C for 5 h [13]. Efimov et al. synthesized phase-pure La_2NiO_4 at 950 °C using nitrate precursors as well as ethylenediaminetetraacetic acid (EDTA) and citric acid as complexing and gelating agents [14].

Poly (vinyl alcohol) (PVA) solution polymerization method has been used successfully to synthesize various monophase, fine, and pure mixed-oxide powders [15–19], but no literature reported the synthesis of La_2NiO_4 by PVA method. In present paper, a method based on polyvinyl alcohol is used to prepare La_2NiO_4 powders. The effect of PVA content on the formation of La_2NiO_4 was investigated. Single-phase La_2NiO_4 was obtained with M/OH = 1:3 at 900 °C.

2. Experimental

La_2NiO_4 sample was synthesized via PVA route. La_2O_3 powders (99.999%), $Ni(NO_3)_3\cdot 6H_2O$ (98.5%), PVA and 65–68% nitric acid were employed as the starting ingredients. A

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5% PVA solution was made by adding PVA (MW = 79,000) to deionized water. The polymer was dissolved by stirring at 70 °C. La_2O_3 powders were dissolved in nitric acid to obtain $La(NO_3)_3$ solution. PVA solution was added to $La(NO_3)_3$ solution with stirring at the temperature of 70 °C, then stoichiometric $Ni(NO_3)_3 \cdot 6H_2O$ was added. During the process, the mol ratios of metal ion to hydroxyl groups in polyvinyl alcohol (M/OH) were 1:0.75, 1:1.5 and 1:3, respectively. With continuous heating at 70 °C under constant stirring to evaporate superfluous water, the volume of the solution decreased and the solution viscosity increased continuously. A gel was formed with evolution of NO_x gas resulting from decomposition of nitrate ions. Throughout the process, no signs of precipitation were observed. Then, the sample was removed from the hot plate and heated in an oven at 250 °C for 2 h. During charring process, the sample with M/OH = 1:1.5 and 1:3 swelled and ignited with an evolution of a large volume of gaseous products. Finally, a voluminous porous powders were calcined at 500–1000 °C for 2 h in static air to obtain La_2NiO_4 powders. The powders calcined at 900 °C were pressed into disks, followed by sintering at 1300 °C for 4 h in air.

Thermogravimetric (TG) analysis (Diamond TG/DTA, PerkinElmer Instruments) was used to monitor the decomposition and pyrolysis of the precursor at a heating rate of 10 °C/min in static air. Fourier transform infrared spectroscopy (FT-IR, Vertex 70, Bruker) was used to determine the chemical bonding of the La_2NiO_4 precursor and powders. The phases were identified by powder X-ray diffraction (XRD) using CuKα radiation (X'Pert PRO, PANalytical B.V.). Field emission scanning electron microscopy (FESEM, Sirion 200, FEI) was used to observe the grain size and the morphology of La_2NiO_4 powders. The electrical conductivity of La_2NiO_4 ceramics was measured at room temperature by a dc four-terminal method in air.

3. Results and discussion

Fig. 1 shows the TG curve of La_2NiO_4 precursor with M/OH = 1:3. The weight loss from 30 °C to 300 °C (8%) was due to the dehydration of the precursor. The weight loss (6%) in the temperature range between 300 °C and 570 °C could be assigned to the decomposition of residual organics by oxidation and the release of N_xO_y, CO, and CO_2 gases. The decomposition of $La_2O_2CO_3$ resulted in a small weight loss of 5% between 570 °C and 640 °C. There is no more weight loss above 640 °C.

FT-IR spectra of La_2NiO_4 precursor (M/OH = 1:3) and powders calcined at 900 °C and 1000 °C are illustrated in Fig. 2. For La_2NiO_4 precursor, the broad absorption band around 3454 cm^{-1} is associated with the O–H stretch of intermolecular hydrogen bonds or molecular water. The bands in the frequency range 1493 cm^{-1}, 1380 cm^{-1} and 856 cm^{-1} were assigned to CO_3^{2-} anions [10]. This is consistent with the later XRD: the major phase for precursor is monoclinic $La_2O_2CO_3$. For La_2NiO_4 powder calcined at 900 °C for 2 h, the bands at 667 cm^{-1} and 511 cm^{-1} are typical of the M–O bonds in the K_2NiF_4 structure [20]. The FT-IR spectrum of La_2NiO_4 precursor calcined at 1000 °C for 2 h is almost the same as that at 900 °C.

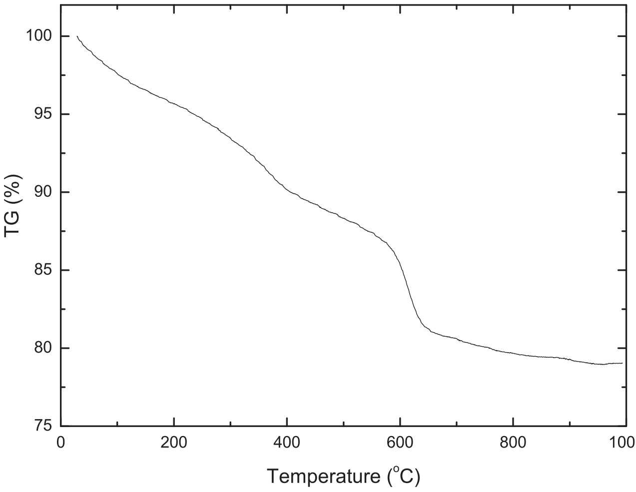

Fig. 1. TG curve of La_2NiO_4 precursor powders with M/OH = 1:3.

Fig. 3 shows the XRD patterns of the La_2NiO_4 precursor (M/OH = 1:0.75) and powders calcined at 500–1000 °C for 2 h. The precursor is XRD amorphous, as is characterized by the broad continuum. The first crystalline intermediates occurred at 500 °C and have been identified as monoclinic $La_2O_2CO_3$ (ICCD file 48-1113), $LaNiO_3$ and La_2NiO_4. After heating the precursor at 600 °C, 700 °C and 800 °C for 2 h, the powder is the mixture of $LaNiO_3$, La_2NiO_4 and $La(OH)_3$. With the temperature increasing, monoclinic $La_2O_2CO_3$ decomposition leads to the formation of $La(OH)_3$. Heating the precursors at 900 °C, $La_3Ni_2O_7$ phase appears and traces of $La(OH)_3$ can still be found. Calcining precursor at 1000 °C, the powder is the mixture of La_2NiO_4 and $La_3Ni_2O_7$, but the diffraction intensity of La_2NiO_4 increases. Pure La_2NiO_4 cannot be obtained from the precursor with M/OH = 1:0.75 at temperature ≤1000 °C.

Fig. 4 shows the XRD patterns of La_2NiO_4 precursor (M/OH = 1:1.5) and powders calcined at various temperatures. Only the diffraction peaks of monoclinic $La_2O_2CO_3$ are found in precursor powders. Calcining the precursor at 500 °C for 2 h, new peaks of La_2NiO_4, $LaNiO_3$ and NiO appear. After heating

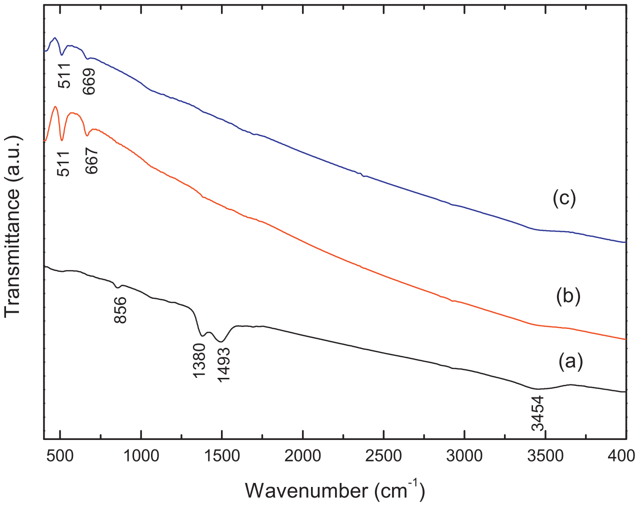

Fig. 2. FT-IR spectra of La_2NiO_4 powders (M/OH = 1:3): (a) precursor, (b) calcined at 900 °C and (c) calcined at 1000 °C for 2 h.

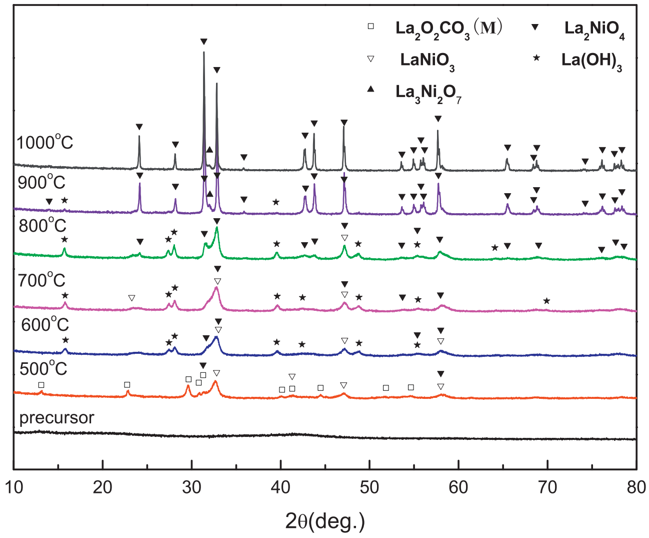

Fig. 3. XRD patterns of La_2NiO_4 precursor (M/OH = 1:0.75) and powders calcined at various temperatures for 2 h.

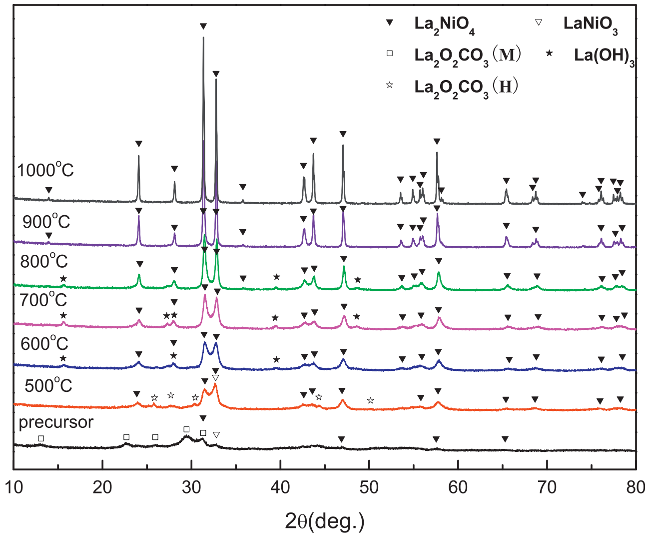

Fig. 5. XRD patterns of La_2NiO_4 precursor (M/OH = 1:3) and powders calcined at various temperatures for 2 h.

the powders at 600–800 °C for 2 h, the peaks of monoclinic $La_2O_2CO_3$ disappear and new peaks of $La(OH)_3$ are found. Heating the precursor at 900 °C for 2 h, the diffraction intensity of La_2NiO_4 increases and the relative intensity of $La(OH)_3$ and NiO decrease, but new phase $La_3Ni_2O_7$ appears. Increasing calcination temperature to 1000 °C, traces of $La(OH)_3$ and $La_3Ni_2O_7$ is still observed. Therefore, single phase La_2NiO_4 was also not obtained from the precursor with M/OH = 1:1.5 at temperature $\leq$1000 °C.

Fig. 5 shows the XRD patterns of the La_2NiO_4 precursor (M/OH = 1:3) and powders calcined at various temperatures. The precursor is the mixture of monoclinic $La_2O_2CO_3$, La_2NiO_4 and $LaNiO_3$. Calcining the precursor at 500 °C for 2 h, the oxycarbonate $La_2O_2CO_3$ (ICCD file 37-0804) is present as a hexagonal phase instead of monoclinic phase. Heating the powders to 600–800 °C for 2 h, the peaks of hexagonal $La_2O_2CO_3$ and $LaNiO_3$ disappear and the powder is the mixture of La_2NiO_4 and $La(OH)_3$. The diffraction peak of La_2NiO_4 is enhanced with increasing temperature. Increasing calcinations temperature to 900 °C for 2 h, single-phase and well-crystallized La_2NiO_4 was formed. The XRD patterns are excellent accord with Refs. [9,11,14] and ICCD file 79-952. After heating the precursor at 1000 °C, the diffraction peaks become stronger and sharper, reflecting greater crystallization. Therefore, it can be concluded that the M/OH ratio is of much importance to the formation of single phase La_2NiO_4. Pure La_2NiO_4 was completely crystallized into orthorhombic structure from the precursor with M/OH = 1:3 at a temperature of 900 °C. In present work, the XRD patterns above 700 °C are similar to that of Ref. [9]. Huang et al. [9] attributed the peak at about $2\theta = 27.5°$ to La_2O_3 and peaks at about $2\theta = 39.5°$ and 48.7° to $LaNiO_3$. However, the strongest peak of La_2O_3 at about $2\theta = 30°$ cannot be found. On the other hand, the XRD patterns at $2\theta < 20°$ was not provided. In Fig. 5, three peaks at $2\theta = 27.5°$, 39.5° and 48.7° are also found along with a peak at $2\theta = 15.6°$. We attribute the impurity peaks to $La(OH)_3$ because the peaks match very well with the $La(OH)_3$ (ICCD file 83-2034), furthermore, there is no peak at $2\theta = 15.6°$ in La_2O_3 and $LaNiO_3$.

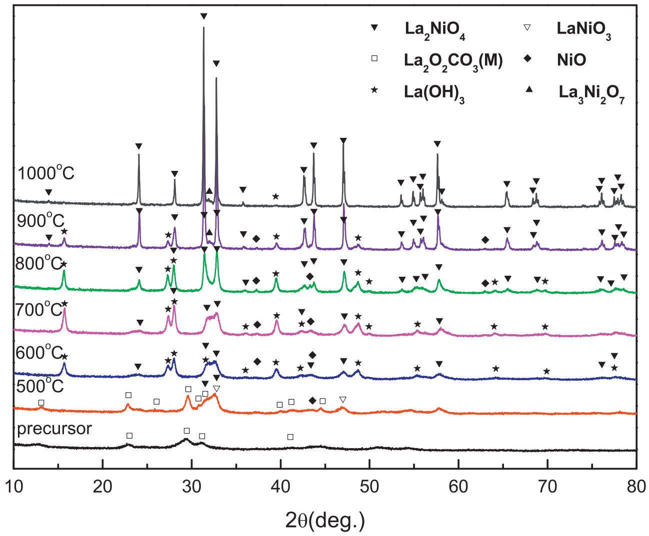

Fig. 4. XRD patterns of La_2NiO_4 precursor (M/OH = 1:1.5) and powders calcined at various temperatures for 2 h.

Fig. 6 shows the field emission scanning electron microscopy micrographs of La_2NiO_4 powders with M/OH = 1:3 calcined at 900 °C for 2 h. The powders are composed of porous networks, which is due to the evolution of a large amount of gases during charring. The particles were agglomerates of smaller primary particles that were about 200 nm. The FESEM images show a uniform grain size distribution and a homogeneous structure.

The main function of PVA is to provide a polymeric network to hinder cations mobility, which maintains local stoichiometry and minimizes precipitation of unwanted phase. In aqueous PVA solutions, many metals can be stabilized at the polymer via interactions with OH groups [15]. As Gulgun et al. [15] stated, the stabilization of the cations in the precursor is established not only through the chemical binding of cations with the functional groups, but also through the physical entrapment of the metal ions in the network of the dried polymer carrier. For

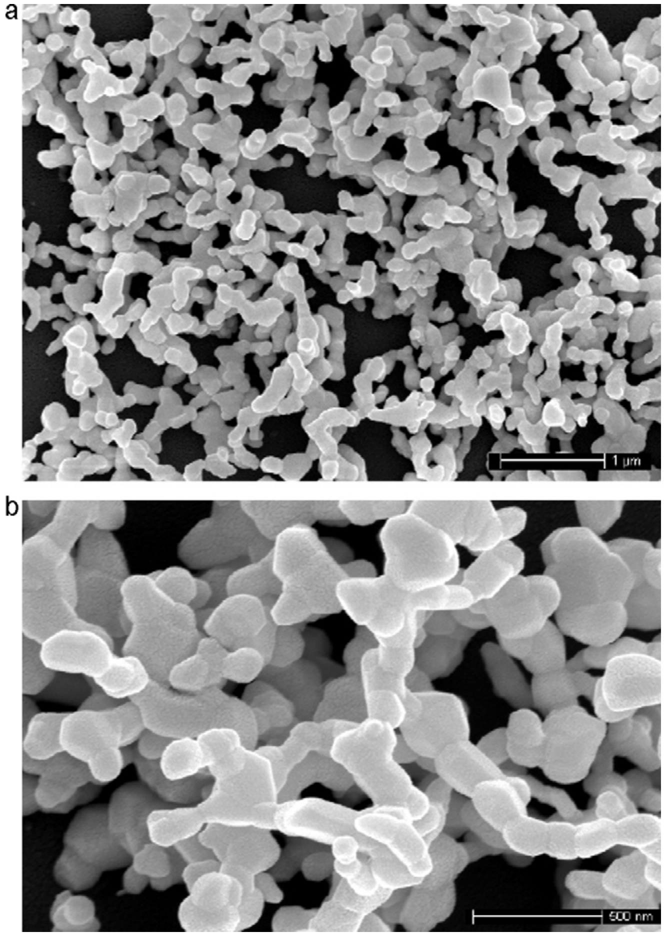

Fig. 6. FESEM micrographs of La_2NiO_4 powders with M/OH = 1:3 calcined at 900 °C in two different magnifications.

precursor with M/OH = 1:3, there were more functional groups (OH groups) in the polymer than cations in the precursor solutions. The chemical linking is stronger than physically stable manner, the homogeneity of precursor with M/OH = 1:3 is higher than that of precursor with M/OH = 1:0.75 and 1:1.5. Therefore, pure La_2NiO_4 was obtained from precursor with M/OH = 1:3.

La_2NiO_4 ceramics sintered at 1300 °C for 4 h shows a linear shrinkage of 18.2%. At room temperature, the La_2NiO_4 ceramic exhibits an electrical conductivity of 42.5 Ω^{-1} cm^{-1}, which is consistent with that reported in Ref. [9].

4. Conclusions

Pure phase La_2NiO_4 was formed by a PVA based method using a M/OH = 1:3 molar ratio after calcination at the temperature of 900 °C, with $La_2O_2CO_3$, $La(OH)_3$ and $LaNiO_3$ as intermediate phases. For the precursors with M/OH = 1:0.75 and 1:1.5, single phase La_2NiO_4 was not obtained at temperatures <=1000 °C. La_2NiO_4 ceramics exhibits an electrical conductivity of 42.5 Ω^{-1} cm^{-1} at room temperature.

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