

Low-temperature synthesis of nanocrystalline NiO–YSZ powders by succinic acid-assisted combustion

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Abstract

Nanocrystalline composite powders, NiO–YSZ were prepared by the succinic acid-containing gel-combustion method at a temperature as low as 310 °C. FT-IR, XRD, DTA/TGA, SEM and TEM were employed to characterize the thermal decomposition of the precursor and the phase evolution and morphology of the calcined powders. The results of FT-IR and thermal analysis showed that the pyrolysis of the precursor began at 171 °C followed by the decomposition of carbonate-containing residues at 245 °C and finally the removal of all pyrolyzed species was completed at 302 °C, accompanied by the crystallization of the metallic nickel, NiO and cubic YSZ phases. The examination of TEM also showed that the nanocrystallites were closely bonded and homogeneously distributed at the nanometric scale.

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1. Introduction

Solid oxide fuel cells (SOFCs) are a promising alternative system of power generation to traditional mobile and stationary sources, such as internal combustion engines and coal-burning power plants, due to their high conversion efficiency of chemical energy to electric power and environmentally friendly nature. However, some material-related problems need to be overcome before SOFCs may be commercialized. For example, metallic Ni is an excellent electrocatalytic media for hydrogen, but the mismatch in thermal expansion with the yttria-stabilized zirconia (YSZ) electrolyte means that it cannot be used directly as an anode of SOFCs. In order to alleviate the mismatch between Ni and YSZ, the Ni particles were usually incorporated into a YSZ matrix to form a cermet, which enables it to be compatible with other components of the SOFCs.

Conventionally, Ni/YSZ cermet is made from YSZ and NiO powders. Subsequently, NiO is reduced to metallic Ni while exposed to fuel in SOFCs [1]. However, the inhomogeneous distribution of Ni particles in the cermet and the subsequent

coarseness of Ni grains at the high cell-operating temperatures of 800–1000 °C may lead to the poor performance of SOFCs [1,2]. Although such a sintering reaction among Ni particles cannot be avoided completely, it may be substantially depressed by utilizing well-mixed nano-sized Ni/YSZ powders [3].

To date, various techniques to prepare Ni/YSZ nanopowders have been proposed such as co-precipitation, mechanofusion and spray pyrolysis [4–6]. However, these methods need expensive apparatus or find it difficult to yield the target powders with accurate stoichiometry.

Gel-combustion method has thus been widely used to synthesize zirconia-based powders [7–12] because of its inherent merits over other methods, including its relatively low cost, simple processing and good control of composition stoichiometry. Besides, in a typical gel-combustion process, the large amount of heat released from the violent combustion reaction between nitrate anions and organic species may promote the formation of the target oxide at a relatively low temperature. Therefore, in the present study, a modified succinic acid-containing gel-combustion method was employed to synthesize the NiO/YSZ composite nanopowders. Succinic acid (C₄H₆O₄) is not only fuel but also a good chelate agent and able to form a stable polymeric precursor with metal ions. Thus, the aim of this study was focused on (i) the effect of the addition of succinic acid on the

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homogeneity of the precursor, (ii) the dependence of the phase evolution of the precursor on calcination temperatures and (iii) the effect of cofiring on the microstructure of the prepared composite powders.

2. Experimental procedure

2.1. Precursor preparation

In this work, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%, J.T. Baker), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Alfa Aesar), $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (99%, SHOWA) and succinic acid (99.5%, Fluka) were used to synthesize the NiO–8YSZ composite nanopowders. Due to the hygroscopic nature of nitrates, in order to control precisely the composition of the prepared precursors, the concentration of cations in the starting materials used in this work was determined by the thermogravimetric analysis. The preparation procedure is described as follows: nitrate salts and succinic acid were separately dissolved in deionized water under stirring. Subsequently, both solutions were mixed together. The mole ratio of metal nitrates used is 205 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$:16 $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$:92 $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and the concentration of zirconium salt and succinic acid in the resultant solution is 0.0314 and 0.0783 M, respectively. The well-mixed solution was then heated at 120 °C. A gelation took place after about 2 h, indicated by a color change from transparent sol to an opalescent but macroscopically homogenous gel. The gel was continuously dried at 120 °C until the dried precursor was obtained.

2.2. Sample characterization

2.2.1. FT-IR analysis

The dried precursor or calcined powders were well-mixed with KBr and pressed into pellets. Spectral measurements were carried out by using a FT-IR spectrometer (JASCO FT/IR-460 plus) that was operated in the transmittance mode. Spectra were normally acquired with the 2 cm^{-1} resolution over the wavenumber range of 400–4000 cm^{-1} . All data were corrected for KBr background spectrum.

2.2.2. Thermal analysis

The thermal decomposition of the precursor was analyzed by simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) (Setaram Setsys Evolution 16/18) in the temperature range from room temperature to 1000 °C in air with a heating rate of 5 °C min^{-1} .

2.2.3. Phase identification

The phase identification of the prepared powders calcined at different temperatures was characterized by X-ray diffraction (XRD) (Rigaku Rad II diffractometer) using $\text{Cu K}\alpha$ radiation in the 2θ range from 15° to 75° with a speed of 4 °C min^{-1} .

2.2.4. Morphology observation

A scanning electron microscope (SEM) (Philips XL-40 FEG) and a transmission electron microscope (TEM) (Philips Tecnai G2 FEG-TEM) operating at 200 kV were used to examine the

morphology and microstructure of the prepared powders. Electron diffraction (ED) was also conducted on the same samples.

3. Results

3.1. FT-IR analysis of the precursor containing succinic acid

Fig. 1 shows the FT-IR spectra of succinic acid, nickel nitrate and complex metal nitrates–succinic acid precursors. In the case of succinic acid (Fig. 1(a)), the bands located at 915 and 1416 cm^{-1} correspond to the out-of plane and in-plane bending vibration of the hydroxyl groups. The bands at 1690 and 1731 cm^{-1} are assigned to the hydrogen bonded and free C=O stretch, respectively. And the bands occurring at 1175 and 1308 cm^{-1} are due to C–C and C–O stretch [13–16]. On the other hand, for nickel nitrate sample (Fig. 1(b)), the bands located at 1371 and 1585 cm^{-1} are attributed to symmetric and asymmetric stretching vibration of the nitrate groups, respectively [17,18].

Fig. 1(c) shows the FT-IR spectrum of the complex nickel nitrate–succinic acid precursor. A few changes were seen in comparison with that of pure succinic acid. It was found that the bands at 1690 and 1731 cm^{-1} , assigned to the C=O stretch of succinic acid, disappeared and some new bands located at

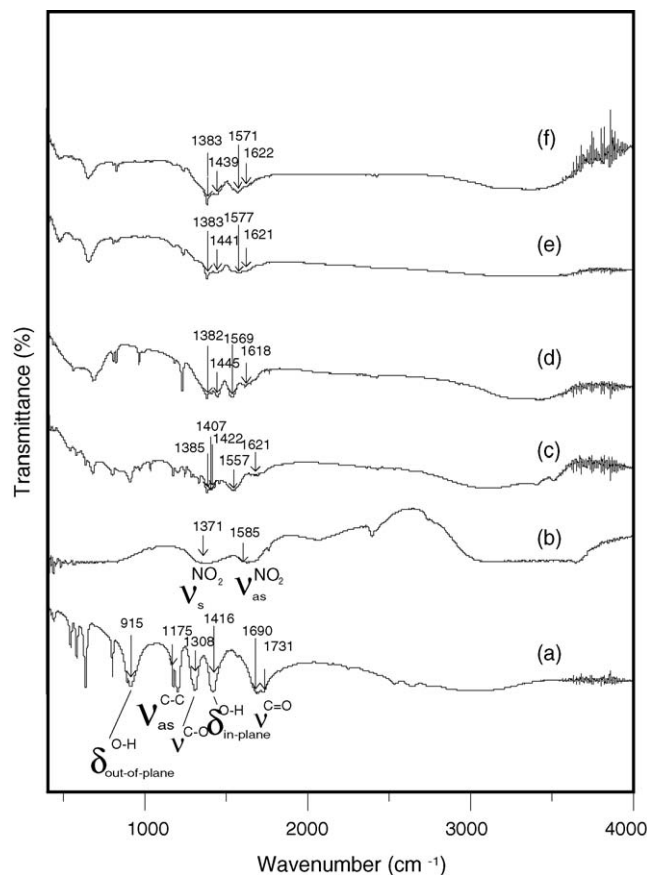


Fig. 1. FT-IR spectra of: (a) succinic acid; (b) nickel nitrate; (c) nickel nitrate–succinic acid; (d) yttrium nitrate–succinic acid; (e) zirconium oxynitrate–succinic acid; (f) (Ni/Y/Zr) nitrates–succinic acid precursors.

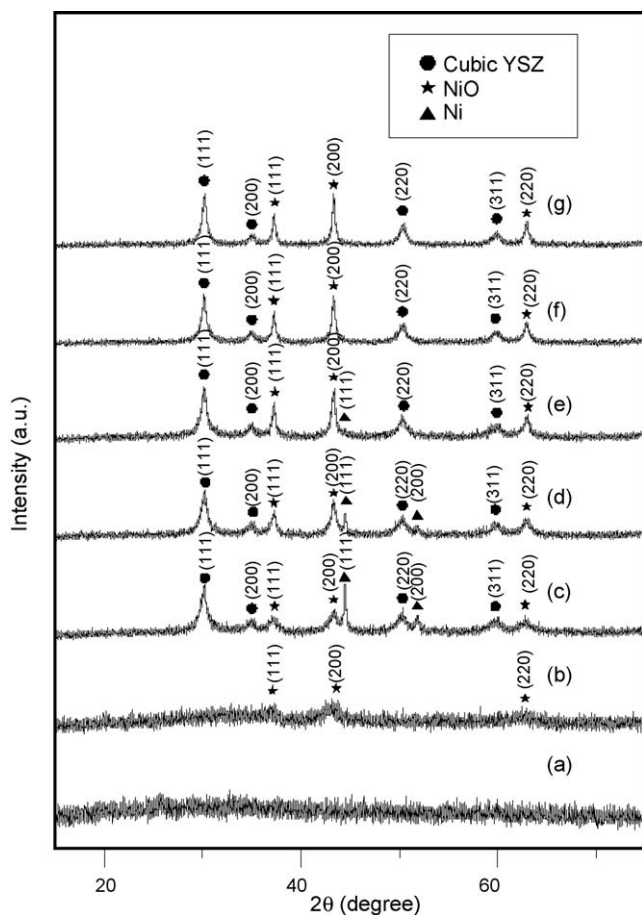


Fig. 4. XRD traces of (Ni/Y/Zr) nitrates–succinic acid precursor after being calcined at: (a) 230 °C; (b) 285 °C; (c) 310 °C; (d) 400 °C; (e) 500 °C; (f) 600 °C; (g) 700 °C for 4 h.

away while an apparent decrease in the bands of nitrate groups was also observed. For the sample calcined at 310 °C for 4 h, all the existing bands were no longer observed, indicating that the thermal decomposition of the (Ni/Y/Zr) nitrates–succinic acid precursor was completed at a temperature of 310 °C.

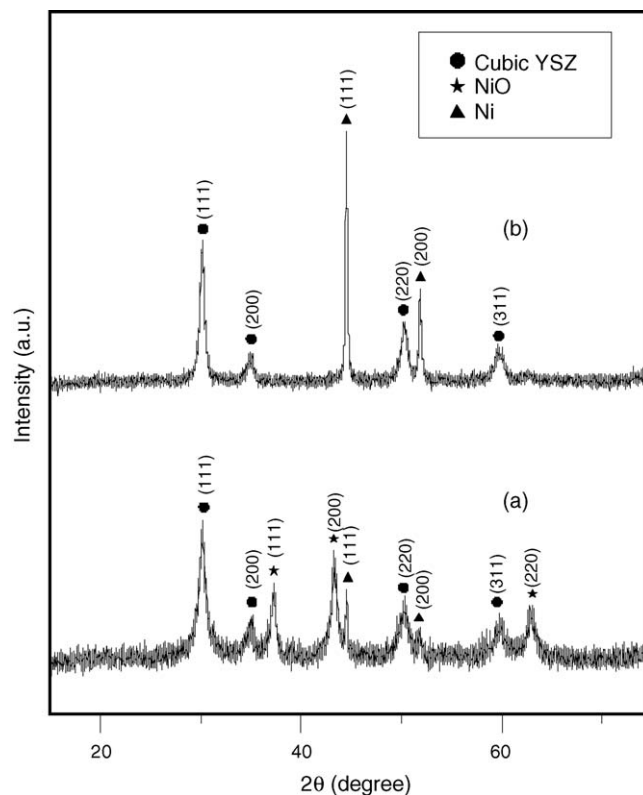


Fig. 5. XRD traces of: (a) (Ni/Y/Zr) nitrates–succinic acid precursor after being calcined at 400 °C for 4 h; (b) 400 °C-calcined powder after being heat-treated at 800 °C for 24 h under a H₂ 20% v/v–Ar atmosphere.

3.2.3. X-ray diffraction analysis

Fig. 4 shows the XRD traces of (Ni/Y/Zr) nitrates–succinic acid precursor calcined at various temperatures. It was found that the calcined precursors were amorphous when the calcination temperature was below 230 °C. With the temperature increasing to 285 °C, some weak diffraction peaks appeared and can be assigned to NiO phase (JCPDS 78-0643). After being calcined at 310 °C for 4 h, the XRD trace showed the presence of the metallic Ni, NiO and cubic YSZ phases. Then, the metal-

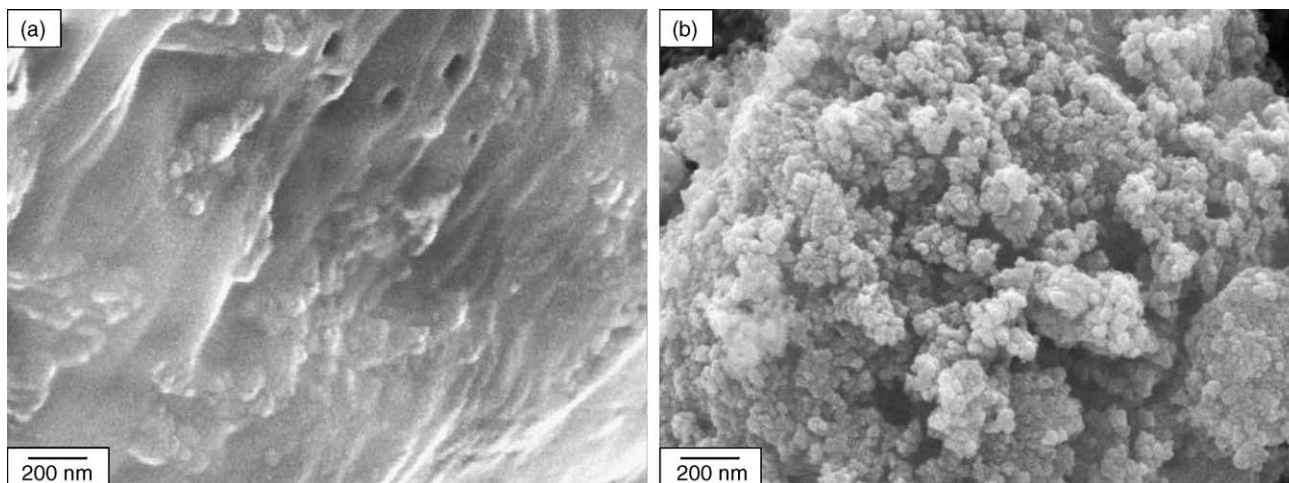


Fig. 6. SEM micrographs of: (a) as-prepared precursor and (b) composite powders calcined at 400 °C for 4 h.

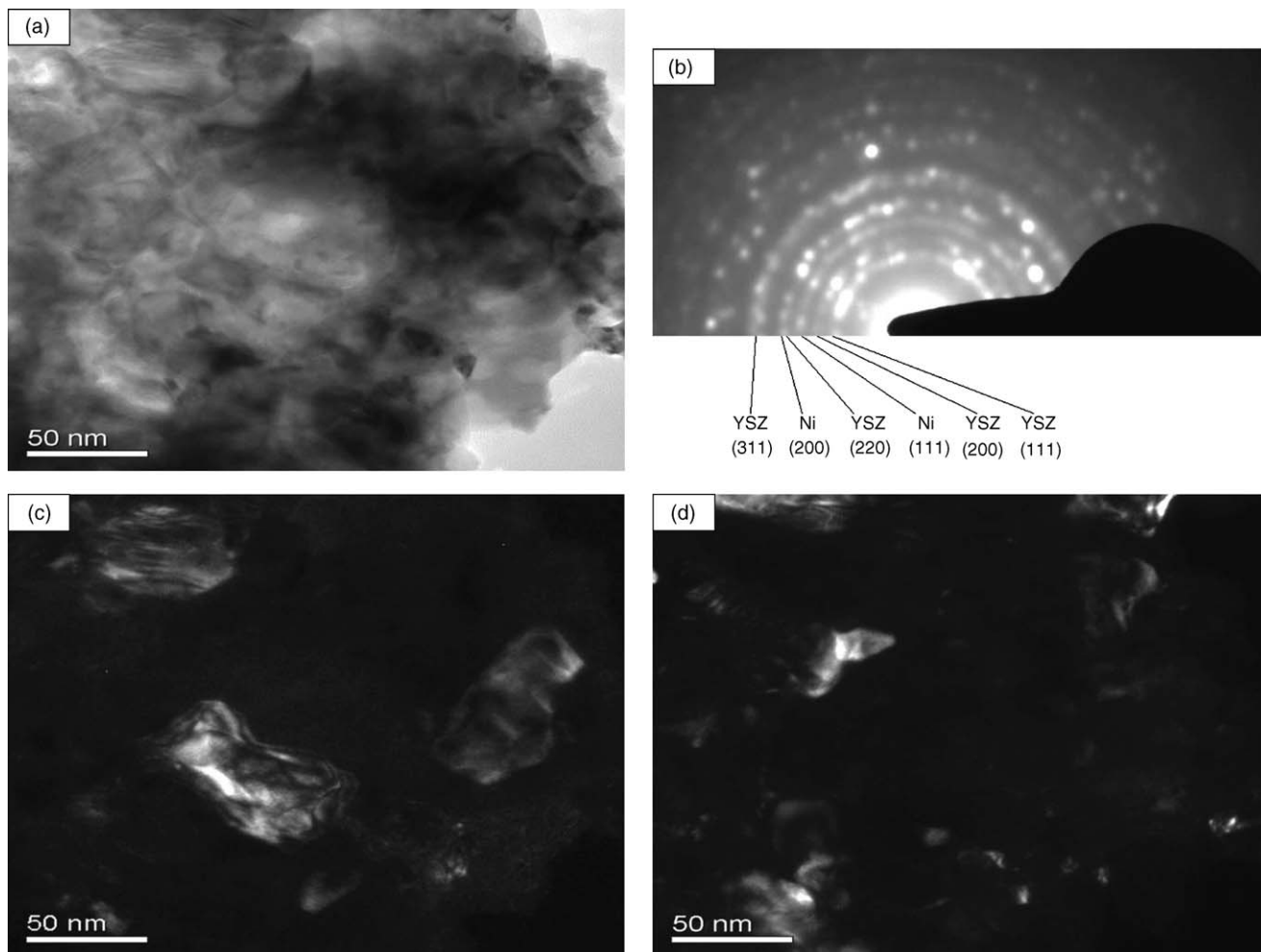


Fig. 7. TEM images of 400 °C-calcined powder after being heat-treated at 800 °C for 24 h under a 20% v/v H₂–Ar reducing atmosphere: (a) bright-field image; (b) electron diffraction patterns and dark-field images corresponding to: (c) cubic YSZ and (d) Ni on the same area.

lic Ni phase further oxidized to NiO when being calcined at 500 °C. At a temperature of 600 °C, no Ni phase was observed, indicating that all residual Ni was completely oxidized to NiO.

3.2.4. Reduction of NiO grains

In order to convert NiO to metallic Ni, a reduction process was conducted. Under a 20% v/v H₂–Ar atmosphere, the 400 °C-calcined powder was heat-treated at 800 °C for 24 h and XRD was employed to identify the phases formed. As is seen in Fig. 5(b), in addition to the cubic YSZ phase, the reflections assigned to the NiO phase disappeared, accompanied by the further growth of the diffraction peaks of the Ni phase. This result indicated that the initially existing NiO has been reduced to Ni under such a reduction process.

3.3. Microstructure observation

Scanning electron micrographs of as-prepared precursor and 400 °C-calcined powders are depicted in Fig. 6. As is seen in Fig. 6(a), the as-prepared precursor showed a glassy surface,

which may be attributed to the nature of the polymeric precursor. After being calcined at 400 °C for 4 h, the morphology exhibited a significant change. It was observed that the agglomerates were made of tiny crystallites with a few tens of nanometer in size. A lot of pores and voids were also observed in the agglomerates, which may be caused by the gases released during the combustion process.

A transmission electron microscopy (TEM) observation was also conducted on the 400 °C-calcined powders after being heat-treated at 800 °C for 24 h under a 20% v/v H₂–Ar atmosphere. Fig. 7(a) shows the typical bright-field TEM image of the resultant powders. Several nanocrystallites of about 20 nm in size were included in one particle. The selected-area electron diffraction pattern (Fig. 7(b)) shows the presence of both metallic Ni and cubic YSZ, consistent with XRD result in Fig. 5(b). The dark-field TEM images of the same area (Fig. 7(c) and (d)) showed lots of light zones, indicating the location of crystalline YSZ and Ni grains, respectively. This revealed that the YSZ and Ni nanocrystallites were homogeneously distributed in these particles without the formation of any clusters.

4. Discussion

4.1. Chelate between succinic acid and metal ions

Although it has been demonstrated that the zirconia-based powders are able to be synthesized at a low temperature of about 300 °C by gel-combustion method, little attention has been paid to the organic fuel. If the organic fuel that functions as the combustion aid may stabilize the precursor, it is believed that this will be more beneficial to the homogeneity of the prepared precursors. As far as succinic acid is concerned, low pyrolysis temperature (about 210 °C) has made it a good candidate as a combustion aid for gel-combustion process (Fig. 2(a)). Besides, it is known that the carboxylate groups of succinic acid may coordinate with metal ions and lead these cations to be homogeneously trapped in the precursor and subsequently form a stable polymeric network structure. As is seen in Fig. 1, FT-IR analysis provides the evidence for the interaction between succinic acid and metal ions. It was found that the bands at 1690 and 1731 cm^{-1} , assigned to carboxylic groups of succinic acid, disappeared and several newly formed bands located at 1407, 1422 and 1557 cm^{-1} were observed after nickel nitrate was added to succinic acid, as is seen in Fig. 1(a) and (c). This result suggests that Ni ions were dissociated from nitrates and subsequently coordinated with the carboxylate anion (COO^-). Similar phenomena were also observed in the succinic acid precursor containing yttrium nitrate and/or zirconium oxynitrate. Thus, it is inferred that the chelating interaction between cations and carboxylate anions of succinic acid can facilitate these metal ions such as Ni^{2+} , Y^{3+} and Zr^{4+} to be homogeneously trapped in the polymeric precursor and is also beneficial to the formation of the NiO/YSZ powders at a low temperature of 310 °C.

4.2. Conversion mechanism from precursor to NiO–YSZ composite powders

An endothermic peak was observed in the temperature range from room temperature to 140 °C in the DTA curve of the (Ni/Y/Zr) nitrates–succinic acid precursor, which was accompanied by 15% weight loss (Fig. 2(b)). Based on the FT-IR analysis in Fig. 3, it was shown that the IR spectrum of the precursor calcined at 140 °C is nearly identical to that of the as-prepared sample, indicating that no decomposition reaction took place at temperatures below 140 °C. Thus, the weight loss at this step is mainly due to the evaporation of the residual moisture absorbed on the surface of precursor.

With increasing calcination temperature, about 20% weight loss was observed in the temperature range between 140 and 230 °C, accompanied by an endothermic peak at 171 °C (Fig. 2(b)). When the precursor was calcined at 230 °C, the color of the sample changed from light green to gray in comparison with the 140 °C-calcined sample. The FT-IR analysis also showed that the bands attributed to COO^- groups decreased when the calcination temperature was raised from 140 to 230 °C and a newly formed band located at 1315 cm^{-1} , which may be assigned to carbonate anion (CO_3^{2-}), was observed (Fig. 3(b)

and (c)). In addition, according to Fig. 2(a), succinic acid may be decomposed completely at about 220 °C. These results suggest that the heat-treatment at 230 °C led to the pyrolysis of the succinate and the subsequent formation of carbonate-containing species.

With further calcination at 285 °C, the decomposition of the carbonate-containing species formed took place based on the fact that the CO_3^{2-} band at 1315 cm^{-1} disappeared, as is seen in Fig. 3(d). Furthermore, the XRD trace in Fig. 4(b) showed that some broad diffraction peaks appeared. These reflections resulted from the NiO phase (JCPDS 78-0643). Therefore, the further calcination at 285 °C caused the crystallization of the NiO phase and the decomposition of carbonate-containing species formed at the previous stage.

It is noteworthy that a violent exothermic peak at 302 °C appeared, accompanied by about 10% weight loss when the precursor was heated at the temperatures ranging from 285 to 310 °C. With further increase of calcination temperature, no thermal reaction occurred, as is seen in Fig. 2(b). On the other hand, FT-IR analysis in Fig. 3 showed that the bands at 1383 and 1540 cm^{-1} due to the nitrate groups disappeared when the temperature was raised to 310 °C. This result indicates that the heat-treatment at the temperature of 310 °C may lead to the decomposition of nitrates involved in the precursor. Moreover, the XRD trace in Fig. 4(c) also showed the presence of metallic Ni and cubic YSZ, in addition to the previous NiO phase. Based on the above results, a large amount of heat released from the combustion reaction led to the further crystallization of the Ni, NiO and cubic YSZ phases and complete decomposition of the residual pyrolyzed precursor.

4.3. Effect of cofiring on the microstructure of composite powders

As mentioned in previous sections, the performance of SOFC was strongly dominated by the distribution of Ni particles in the cermet. Thus, in order to examine the homogeneity of NiO/YSZ composite powders obtained from gel-combustion method in this work, TEM was employed to observe the microstructure of the 400 °C-calcined powders after being heat-treated at 800 °C for 24 h under a 20% v/v H_2 –Ar atmosphere. Based on the bright-field TEM image in Fig. 7(a), it was found that several nano-sized grains were included in one particle. These grains are assigned to the metallic Ni and cubic YSZ phases, as is evidenced from the result of the ED pattern in Fig. 7(b). In order to locate these corresponding phases, a TEM dark-field image was also conducted on the same sample, as shown in Fig. 7(c) and (d). It is seen that the grains assigned to Ni and YSZ phases were closely bonded to each other and beneficial to the formation of a continuous network structure. Thus, it is believed that the NiO/YSZ powders obtained by gel-combustion method in this work may effectively extend the triple-phase boundary and promote the performance of SOFC when they are employed to fabricate the anode of SOFC.

5. Conclusions

Based on the results of this work, the following conclusions may be drawn:

1. The pyrolysis of the succinic acid precursor containing nitrates was a function of the calcination temperatures. The decomposition of the precursor began at 245 °C and subsequently a violent exothermic reaction took place at 302 °C. It led to the complete removal of the pyrolyzed residues and nitrates.
2. All Ni/Y/Zr ions were trapped homogeneously in the polymerized precursor at the molecular scale via coordination with the carboxylate groups of succinic acid. This results in the simultaneous formation of metallic Ni, NiO and YSZ at the low temperature of 310 °C.
3. The phases of the prepared powders strongly depended on the calcination temperatures. The presence of metallic Ni, NiO and YSZ was observed when the precursor was calcined at 310 °C for 4 h. With the temperature increasing to 600 °C, the metallic Ni completely oxidized to NiO.

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