

Short communication

Synthesis of nano-crystalline (Ni/NiO)–YSZ by microwave-assisted combustion synthesis method: The influence of pH of precursor solution

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Abstract

Microwave-assisted combustion synthesis can be used to synthesize the nano-crystalline (Ni/NiO)–YSZ composites. In this study nano-crystalline powders were prepared by combustion synthesis process in a microwave oven. The influence of pH value of the precursor solution on the combustion behavior and phase formation of synthesized powders were investigated by X-ray diffraction technique (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermal analysis (DTA/TGA), infrared (IR) spectroscopy, and BET surface area analysis. The results show that by increasing pH value, the combustion rate decreases. The as-burnt powder prepared with pH 0.5 has a higher crystallite size (32 nm). Furthermore, FTIR studies show that the glycine monodentate complex convert to bidentate complex with increasing pH.

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1. Introduction

Solid oxide fuel cells (SOFC) are of current interest as energy conversion system owing to their high efficiency and environmentally friendly nature [1]. Main three component of SOFC are electrolyte, cathode and anode. The most frequently used SOFC system employs yttria-stabilized zirconia (YSZ) as an electrolyte, cermet like nickel–YSZ as an anode and $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ ($\text{M} = \text{Sr}, \text{Ba}$) or LaCoO_3 as a cathode [2]. The requirements of the anode material are high electronic conductivity, thermal expansion compatibility with other SOFC component and porous microstructure [1].

Nickel–YSZ cermet is usually made from YSZ and NiO powder. NiO is then reduced in situ to nickel metal when exposed to the fuel in SOFC [1]. It has been shown that preparation technique is very important factor in controlling the stability and performance [3].

Among the various methods, solution combustion synthesis seems to be versatile. This method is quite simple and does not involve multiple steps. With solution process atomic level doping and homogeneity can be achieved [4]. The solution com-

bustion method utilizes the exothermic reaction between metal nitrates (oxidizer) and fuel [5].

Researchers have demonstrated the use of microwaves in combustion synthesis and found several advantages for the synthesis of many organic and inorganic materials compared to conventional methods [6,7]. The foremost of these advantages are the short time periods for the synthesis, enhanced reaction kinetics, and the reactant selectivity during energy transfer from the microwave field that assists the stabilization of the metastable phase of the material. Therefore, it is possible to control both the kinetic and thermodynamic factors of the chemical reactions using microwaves in the combustion process.

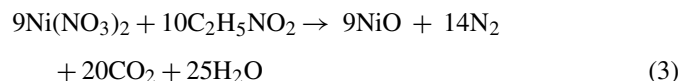
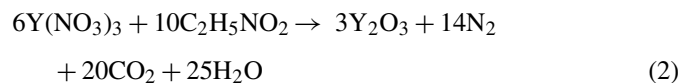
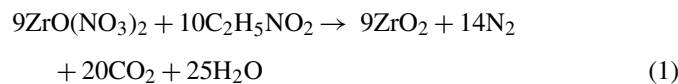
In this study, we synthesize nano-crystalline (Ni/NiO)–YSZ composite powders and investigate the influence of pH value of solution on combustion process and powder characteristics.

2. Experimental

$\text{ZrO}(\text{NO}_3) \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.9%), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99.9%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (BDH, 99%) and glycine (Merck, 98.5%) were used for the synthesis of composites. The precursor solution was prepared by dissolving and mixing the required amount of the metal nitrates in distilled water so that the reduced composite contain 40 vol.% Ni and 60 vol.% 8YSZ.

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Glycine was then added into the prepared aqueous solution. The molar ratio of metal nitrates to glycine was calculated according to the following formulas:



The initial pH of mixed solution was about 2. A low amount of ammonia was added to the solution to adjust the pH value to about 3, 5 and 9. Also, a solution with pH value equal 0.5 was prepared by adding nitric acid. During the procedure, the solution was continuously stirred using a magnetic agitator. The solution was evaporated by heating at 85 °C with continuous stirring until a viscous gel formed. Then the viscous gel was put in a microwave oven (Panasonic, 2.45 GHz, 1000 W, 40 L). After a few seconds the dried gel burnt in a self-propagating combustion manner until the gels were completely burnt out to form a voluminous mass.

The dried gel precursors were characterized via thermogravimetric (TGA) and differential thermal analysis (DTA) (PL-STA-1640) at a heating rate of 10 °C min⁻¹ in static air. Infrared spectra (IR) for the gel precursors were recorded on a Bruker (V33) spectrophotometer from 400 to 4000 cm⁻¹ by the KBr pellet method. XRD (Siemens D-500, $\lambda_{\text{K}\alpha\text{Cu}} = 1.5418 \text{ \AA}$) was used for phase analysis and crystallite size determination of burnt powder. Crystallite size was calculated from Scherrer's equation:

$$t = \frac{0.9\lambda}{\sqrt{(B^2 - b^2)\cos\theta}}$$

where B is the half value breadth (rad), b is the half value breadth for materials of which crystallite size larger than 100 nm, λ is the X-ray wavelength (nm), t is the average of crystallite size (nm) and θ is the diffraction angle [8]. The morphology of the powders were investigated by scanning electron microscopy (SEM, XL30-Philips) using secondary electron imaging and transmission electron microscopy (TEM, CM200FEG-Philips) in the bright field mood. Specific surface area was measured by BET method (Micrometrics Gemini 2375 instrument).

3. Results and discussion

The experimental observations showed that when the gels were ignited, the combustion process rapidly propagated forward until all the gels were burnt out completely to form loose powders. It was also observed that the combustion rate was significantly influenced by the pH value of the mixed solution. With increasing pH value from 0.5 to 9, the combustion rate

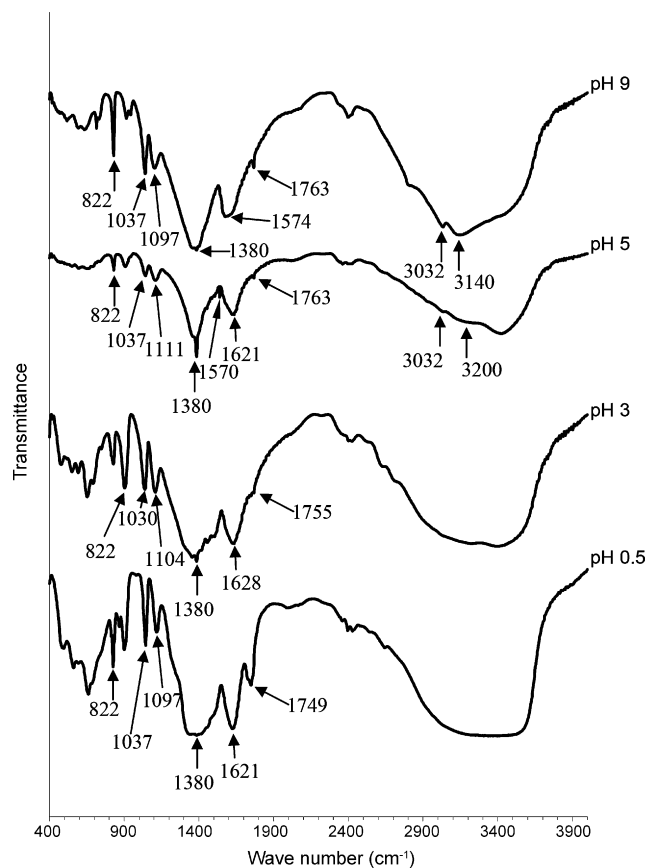


Fig. 1. FTIR spectra of dried gel prepared at pH 0.5, 3, 5 and 9.

decreased and the librated gases increased significantly. The precursor which prepared in the acidic condition took a long time to ignite whereas precursors with basic conditions ignited in a few seconds. Microwave heating in contrast with traditional method depends on energy conversion in polar molecule [9]. Because of the high concentration of polar molecule (OH^- and NH_3) at basic pH, microwave absorption increases and ignition time decreases.

IR spectra of the dried gels were examined to investigate the chemical and structural changes that take place during the combustion process. Fig. 1 shows the IR spectra for dried gels prepared at pH 0.5, 3, 5 and 9 in the range 400–4000 cm⁻¹. It is clearly seen from the figure that the dried gels show absorption bands at 1380 and 822 cm⁻¹ corresponding to the NO_3^- and ZrO^{2+} ions, respectively [10]. The appearance of the characteristic bands of NO_3^- indicates that the NO_3^- exists as a group in the structure of gel during the gelation of mixed solution formed from nitrates and glycine. The rocking vibration of glycine NH_2 group is the cause of absorption bands at about 1100 and 10356 cm⁻¹ [11].

The absorption bands at about 1620 and 1750 cm⁻¹ in IR spectra of dried gel prepared at pH 0.5 correspond to the deformation vibration of NH_2 and stretching vibration of $\text{C}=\text{O}$, respectively [11]. Presence of $\text{C}=\text{O}$ stretching vibration at about 1750 cm⁻¹ indicates the presence of COOH group at dried gel [12]. Therefore, simultaneous presence of NH_2 and COOH indicates that glycine coordinates to metal cation as monodentate

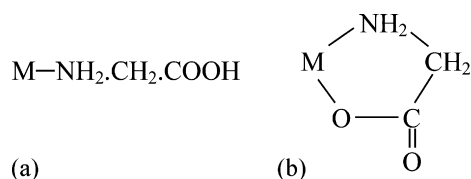


Fig. 2. Glycine coordination to metal atom (a) monodentate and (b) bidentate.

ligand [12] as show in Fig. 2a. With increasing pH (pH 3 and 5), absorption band appear at about 1570 cm^{-1} corresponds to COO^- group which indicates glycine ionization. In IR spectra of dried gel prepared at pH 9, absorption band at 1620 cm^{-1} disappeared, the intensity of absorption band about 1760 cm^{-1} increased and absorption band at 1570 cm^{-1} appeared. The latest corresponds to bidentate ligand of glycine (Fig. 2b) [12].

In order to evaluate the effect of pH value on combustion behavior, the dried gel powders prepared at different pH values were characterized via TGA and DTA at a heating rate of $10^\circ\text{C min}^{-1}$ in static air. Fig. 3 shows the DTA and TG plots of dried gels prepared under different pH values.

It can be seen that the pH value of precursor solution has a significant influence on the decomposition and combustion behavior of gel precursors. The width of exothermic peak of combustion increases by the increase of pH, which suggests that, the rate of reaction decreases [13]. As reported [14], carboxylic ions (COO^-) retard the combustion reaction. Therefore,

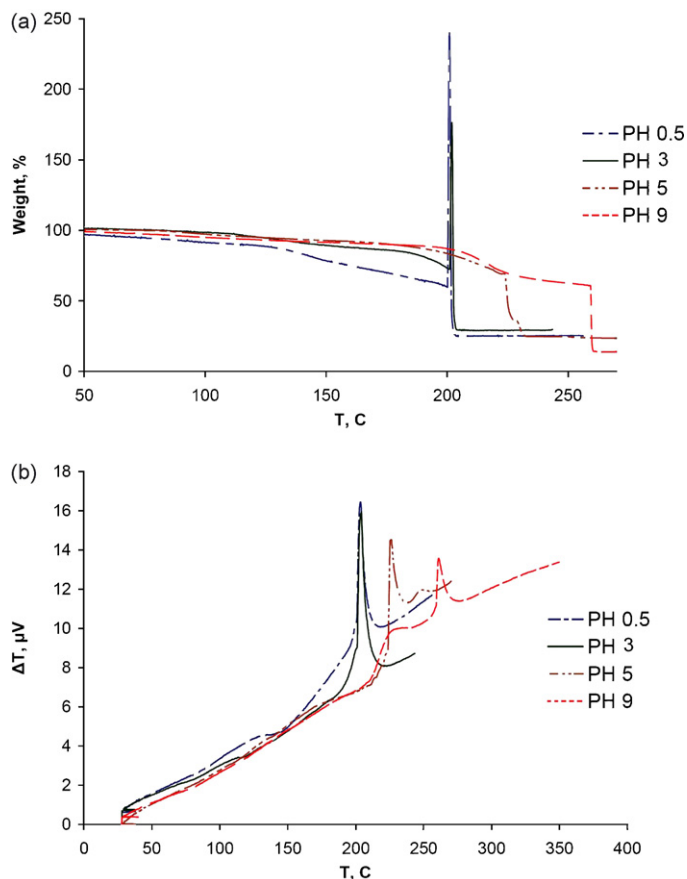


Fig. 3. (a) TG and (b) DTA plot of dried gel prepared at different pH.

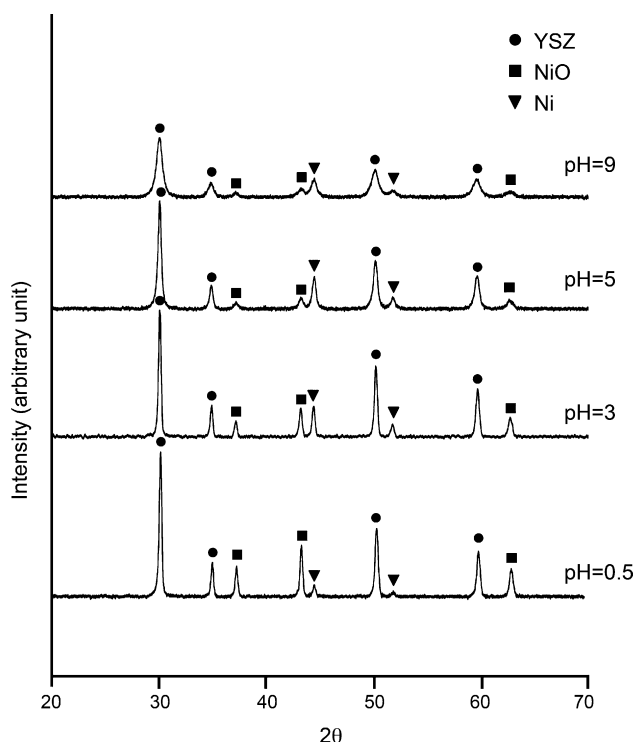


Fig. 4. XRD patterns of as-burnt powder prepared with different pH.

decreasing in reaction rate at basic pH is due to the presence of COO^- ions. Also, it can be seen that by increasing pH, ignition temperature increases. Bidentate ligands need more energy for decomposition rather than monodentate ligands; therefore combustion at higher pH was accomplished at a higher temperature.

The precursors prepared at pH 0.5 and 3 show a sharp peak in their TG plot at ignition temperature, which is due to the exothermic reaction force. In contrast, the precursors prepared at pH 5 and 9 do not show such feature, that confirms the weak combustion at basic pH.

Fig. 4 shows the XRD patterns of as-burnt powder prepared at different pH. It is clear that all of powders are crystalline and consist of three phases: YSZ, NiO and Ni. Calculations show that the crystallite size of each phase decreases with the increase of pH (Table 1), which is due to the weak combustion and low heat generation at the higher pH. Fig. 5 shows TEM images of the powder prepared at different pH that confirms the decrease of crystallite size with the increase of pH.

The typical SEM image of as-burnt powders is represented in Fig. 6, which exhibits highly agglomerated particles having porous feature, due to the liberation of large amount of gas during combustion.

Table 1
Crystallite size of various phase calculated from Scherrer's equation

Phase	Average crystallite size (nm)			
	pH 0.5	pH 3	pH 5	pH 9
YSZ	32	28	24	13
NiO	33	28	17	8
Ni	33	28	23	15

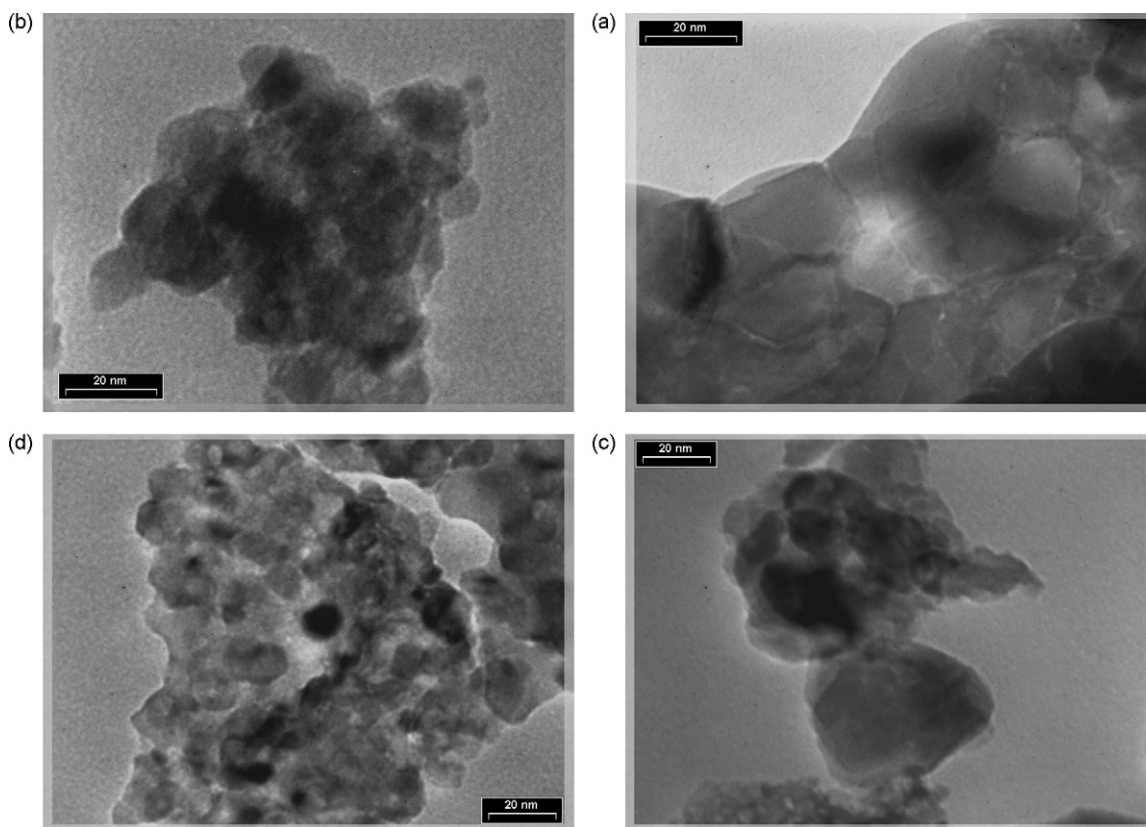


Fig. 5. TEM images of powders prepared with different pH: (a) pH 0.5, (b) pH 3, (c) pH 5 and (d) pH 9.

BET analysis reveals the increase of pH leads to the increase of specific surface area from 4 to 16 $\text{m}^2 \text{g}^{-1}$ (Fig. 7). The observed behavior can be attributed to the contribution of ammonia in the combustion reaction and producing more gas. The flowing out gases dissipates the heat of combustion, thereby preventing the

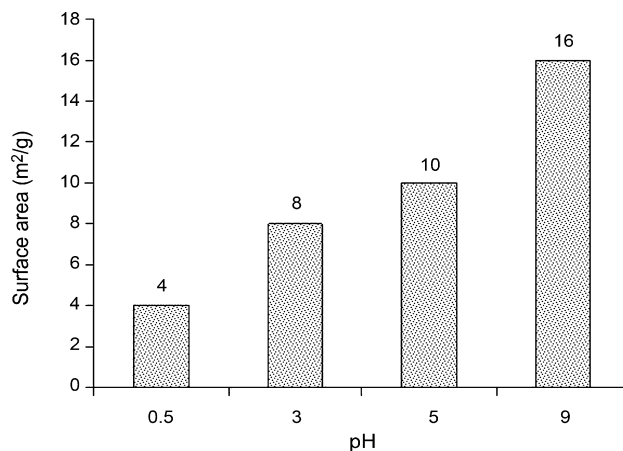


Fig. 7. BET surface area of different powders.

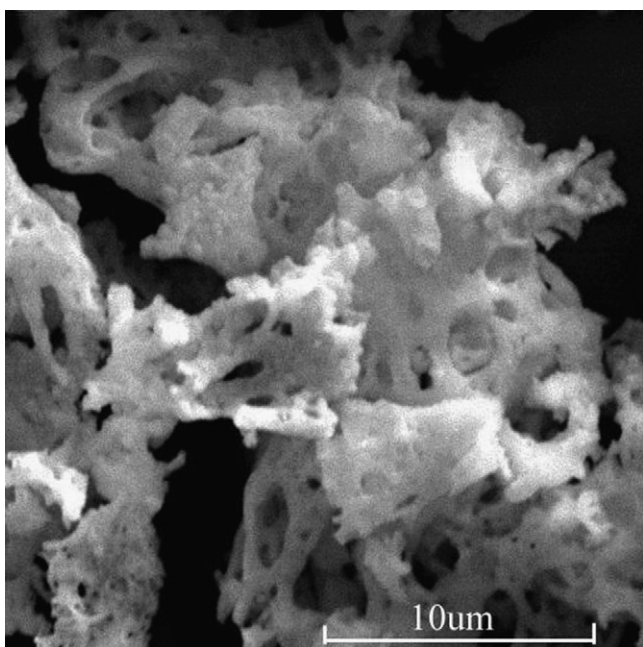


Fig. 6. Typical SEM image of synthesized powder.

sintering of formed oxide powders, as well as cracking of formed agglomerates.

4. Conclusion

Nano-crystalline (Ni/NiO)–YSZ composite was synthesized by microwave-assisted combustion method. The nitrate–glycine gels burnt in a self-propagating combustion way. The experiments conducted in this study suggest that the pH value of the mixed precursor solution has a significant influence on combustion and formation of (Ni/NiO)–YSZ composite. Precursors prepared at acidic pH take a long time to ignite whereas pre-

cursors prepared at basic pH ignite at a few seconds. At acidic pH, glycine coordinates with metal cation as a monodentate ligand and at basic pH, it coordinates as a bidentate ligand. With the increase of pH value the combustion rate and crystallite size decrease and surface area increase. The resulted powders have porous feature because of flowing out of a large amount of gas during combustion.

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