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Synthesis of NiO–ZrO_2 powders for solid oxide fuel cells

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Abstract

With $NH_3{\cdot}H_2O$, $NH_3{\cdot}H_2O$-NH_4HCO_3 buffer solution and NaOH solution as coprecipitation agents, NiO–ZrO_2, anode powder of solid oxide fuel cell, was synthesized by coprecipitation methods. Composition accuracy was analyzed by comparing the original composition with the mass of the eventually obtained powder. It was shown that cubic NiO and cubic YSZ with a cascade powder distribution were obtained after the powder was calcined for 1h at different temperatures. Composition analysis of the powder synthesized with $NH_3{\cdot}H_2O$ as coprecipitation agent showed that NiO–YSZ powder greatly deviated from the original composition due to the loss of Ni^{2+} in the form of $[Ni(NH_3)_4]^{2+}$. When $NH_3{\cdot}H_2O$–NH_4HCO_3 buffer solution was used, productive output of nickel was increased. The loss of nickel can be totally avoided and better control of the powder composition could be realized when NaOH was used as coprecipitation agent.

Keywords: A. Powders: chemical preparation; D. Transition metal oxides; E. Fuel cells; E. Electrodes

1. Introduction

Solid oxide fuel cells (SOFCs) are a kind of developing and promising power generation equipment. According to different synthesis methods of electrolyte, they can be divided into three basic modes: 1) electrolyte-supported cell, 2) cathode-supported cell, 3) anode-supported cell [1]. Taking all kinds of polarization factors and sensitivity of fuel cell components to polarization effects into consideration, performance of an anode-supported fuel cell is optimum [2]. In an Anode-supported cell, the porous anode is used as substrate and the electrolyte and cathode loaded on it. Anode-supported SOFCs are suitable for operating at intermediate temperature because the electrolyte layer can be made extremely thin, typically about 20 μm [3]. By lowering the operating temperature conventional stainless steel can be used as interconnectors or auxiliary components with which high mechanical reliability of a cell-stack and lower manufacturing costs can be achieved. Its superiority lies in lower IR resistance and thinner electrolyte. Anode substrate should fill the following requirements: 1) certain porosity for fuel gas and water vapor flowing in and out; 2) appropriate electrical conductivity, that means proper ratio of Ni to YSZ to keep high catalysis activity and avoid sintering; 3) large active three phase interface, so that the polarization resistance will not increase considerably with the reduction in operation temperature. Concentration polarization maybe increased by gas diffusion due to the anode thickness. The anode substrate should not only hold high electrical activity but also have proper electrode microstructure to reduce concentration polarization and electrochemical polarization.

YSZ was added to the nickel anode for the sake of thermal expansion coefficient mismatch between the nickel anode and the YSZ electrolyte [4]. Conventional method is to mix the powder of YSZ and NiO homogeneously by mechanical way. Ceramic cermet can be obtained after sintering and reduction process. The advantages of conventional mixing are simple manufacture technique and accurate chemical composition. But it may cause inhomogeneity of composition. For anode-supported SOFC, physical mixing may further increase polarization of the anode. This problem can be solved by coprecipitation method. Since Ni volume ratio dominates IR resistance and polarization resistance in anode substrate, the ratio of Ni to YSZ should

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be strictly controlled. Heretofore, the composition accuracy has not been discussed yet in literatures although the coprecipitation method has been investigated to prepare the anode-supported electrolyte composite powders [5]. The purpose of this paper is to synthesize NiO/YSZ anode powder by three different coprecipitation techniques, with an emphasis on controlling the accurate composition.

2. Experiment

Powder compositions were designed to be 30:70, 35:65, 40:60 and 45:55 in volume ratio of Ni/YSZ, while YSZ contained 8 mol% Y_2O_3. Different amounts of $ZrOCl_2\cdot 8H_2O$, Y_2O_3 and $NiCl_2\cdot 6H_2O$ were dissolved into water to make several solutions with concentration of 1 mol/l. Zr^{4+}, Y^{3+} and Ni^{2+} were coprecipitated by three different precipitation agents of $NH_3\cdot H_2O$ solution, $NH_3\cdot H_2O$–NH_4HCO_3 buffer solution and NaOH solution, while keeping stirring and proper pH. After being washed, filtrated 5 times, the composite powders were oven-dried for 4 h at 120 °C. Calcination schedule was determined according to Differential thermal analysis (ZRY-ZP). Crystallization of the oxides was identified by X-ray diffraction using Cu-K_α radiation (XRD, BDX3300) after calcined at 600, 800 and 1000 °C respectively. Microstructure of the powder was investigated using transmission electron microscopy (TEM X-100). Compositions of the powders were analyzed by ICP [ICP-9000 (N + M)]. The composition accuracy was determined through comparing the originally designed composition with the mass of obtained powders.

3. Results and discussion

3.1. Determination of the synthesis technique

Solubility product constants of NiO and ZrO_2 are $K_{sp}(NiO) = 2\times10^{-15}$ and $K_{sp}(ZrO_2) = 3\times10^{-26}$ respectively at room temperature. When 400 ml water was added before titration, it was calculated that both $Ni(OH)_2$ and $Zr(OH)_4$ can be precipitated at pH value of 8.2. The real pH value was kept about 8.5 or a little higher while powder synthesis.

The differential thermal analysis curve of a powder is shown in Fig. 1. There was an endothermic peak and exothermic peak at 299 °C and 548 °C separately. The endothermic peak corresponded to dehydrate process, and the exothermic peak corresponded to oxide crystallization process. According to this, the composite powders were calcined at three different temperatures (600, 800 and 1000 °C) for 1 h in order to find an optimum temperature.

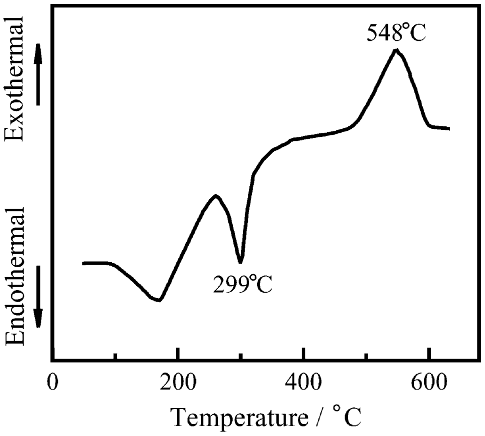


Fig. 1. Differential thermal analysis curve of 40 vol.% Ni/YSZ.

3.2. Crystal phase and microstructure analysis

XRD analysis of different powders calcined at different temperatures showed that cubic NiO and cubic YSZ were obtained for various powder compositions. No second phase was observed. As electron carrier, Ni, reduced from NiO, supplies the anode substrate with considerably large conductivity. With ionic conductor, cubic YSZ, which transfers O^{2-} from electrolyte into anode, active triple boundary area can be expanded from electrolyte/anode boundary to the whole anode substrate and the anode catalystic performance will be enhanced. Fig. 2 shows XRD patterns of 45 vol.% Ni/YSZ calcined at 600, 800 and 1000 °C. It can be seen that crystallization increased with the temperature. It

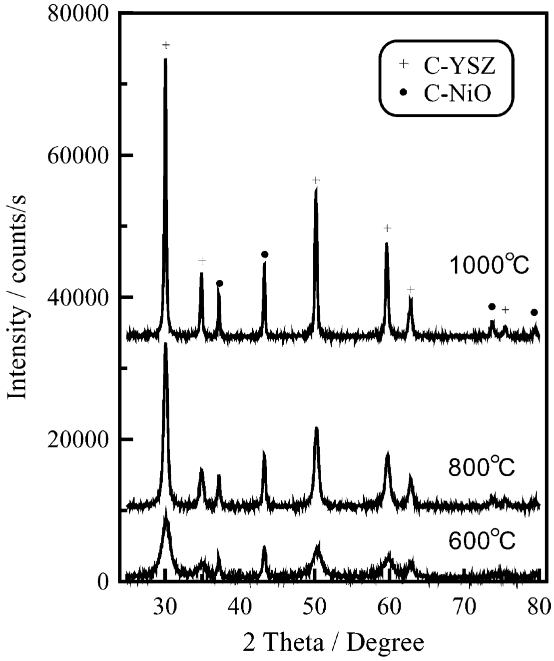


Fig. 2. X-ray diffraction patterns of 45 vol.% Ni–YSZ composite powder.

was completely transformed to cubic phase when the powder was calcined at 1000 °C.

The TEM photographs of 40 vol.% Ni–YSZ calcined at different temperatures are shown in Fig. 3.

It can be seen from the TEM photographs combined with Fig. 2 that the powder calcined at 600 °C was not well crystallized. The morphology of particles was not very clear. It was difficult to be well dispersed by short time grinding, attributed to small grain size with high activity and incompletely broken agglomerates. The diameter of the particles was only 10 nm or so in the distinguishable area. Particles grew a little to 20–30 nm at 800 °C and increased greatly to 60–70 nm at 1000 °C. Different particle distribution can be made after calcined at different temperatures. Adequate specific surface area of oxidation–reduction reaction should be applied for ideal anode substrate, yet too small particles may hamper gas permeation from anode. It is therefore predicted that powders calcined at 800 °C can provide proper microstructure.

3.3. Effect of different coprecipitation agents on powder composition

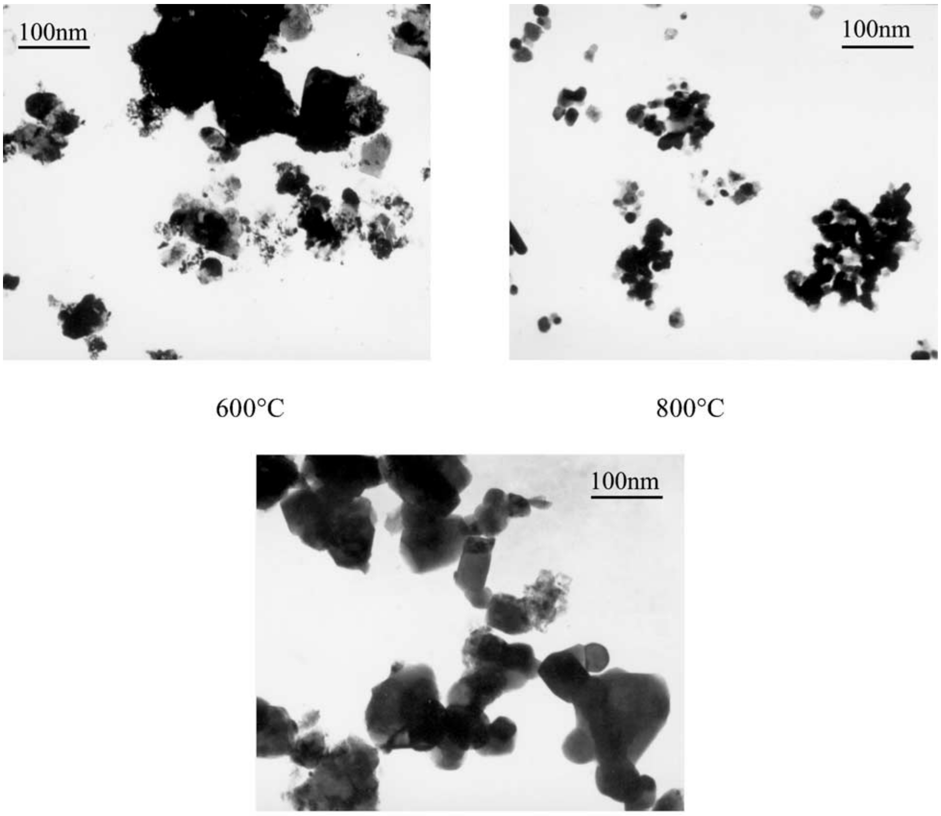
When $NH_3{\cdot}H_2O$ was used as coprecipitation agent, aqueous solution percolated through was blue due to loss of Ni^{2+}. The ratio of NiO to YSZ greatly affected the anode substrate performance, so it is necessary to measure the composition accuracy of the powder. The powder of 40 vol.% Ni–YSZ, as an example, was analyzed by plasma emission spectrum. It was shown that Ni content was only 15.8 wt.%, much lower than the theoretical 44.0 wt.%. Meanwhile, it was verified through mass calculation of the powder. Similar results of low NiO yield for the other compositions were also obtained. Since yield of YSZ was high and stable, we assumed it was 90% in this experiment. The results of mass calculation of other samples are shown in Table 1.

The calculation result was somewhat higher than the detected. It may be due to the real productive rate of

Table 1
Weight analysis of NiO–YSZ powder synthesized with $NH_3{\cdot}H_2O$ as coprecipitation agent based on 100 g Ni–YSZ

Ni (vol.%)	$NiO–YSZ_{(th)}$ (g)	$NiO–YSZ_{(r)}$ (g)	$NiO_{(r)}$ (g)	$NiO_{(th)}$ (g)	NiO yield (%)
30	110.6	64.6	9.6	55.6	17.3
35	112.1	66.4	16.3	62.1	26.3
40	113.6	63	17.8	68.3	26.1
45	115	56.2	15.5	74.3	20.9

$NiO–YSZ_{(th)}$ is the theoretical quantity; $NiO–YSZ_{(r)}$ is the real yield; $NiO_{(r)}$ is the real yield; $NiO_{(th)}$ is the theoretical quantity.



600°C

800°C

1000°C

Fig. 3. TEM photographs of 40 vol.% Ni–YSZ calcined at different temperatures.

Table 2
Weight analysis of Ni-YSZ powder synthesized with NaOH as coprecipitation agent based on 100 g Ni–YSZ

Ni (vol.%)	NiO–YSZ$_{(th)}$ (g)	NiO–YSZ$_{(r)}$ (g)	NiO$_{(th)}$	NiO$_{(r)}$	Yield (wt.%)
45	114.95	110.5	74.32	69.87	94.01
40	113.6	105.84	63.31	60.62	95.74

NiO–YSZ$_{(th)}$ is the theoretical quantity; NiO–YSZ$_{(r)}$ is the real yield; NiO$_{(r)}$ is the real yield; NiO$_{(th)}$ is the theoretical quantity.

YSZ was higher than 90%. Conclusively, the NiO productive rate was very low. The reason for this was the loss of Ni^{2+} due to the following reaction:

$$Ni^{2+} + 4NH_3 \cdot H_2O = [Ni(NH_3)_4]^{2+} + 4H_2O \quad (1)$$

Reaction rate constant of formula (1) is considerably large, 3×10^8. A great deal of Ni^{2+} lost in the form of $[Ni(NH_3)_4]^{2+}$ if the concentration of NH_3H_2O was high. However, if the concentration was low, $Ni(OH)_2$ could not precipitate completely. For anode-supported SOFC, the Ni volume ratio of the anode substrate determines the IR resistance and polarization resistance [6]. The ratio of Ni to YSZ must be strictly controlled. From the above description, $NH_3{\cdot}H_2O$ was not suitable for preparing strictly controlled anode powder, Ni–YSZ.

Then the coprecipitation agent was changed to a buffer solution of $NH_3{\cdot}H_2O$–NH_4HCO_3. The pH value was kept at about 8.5 while synthesizing 40 vol.% Ni–YSZ anode powder. NiO yield increased to 33%, higher than that when $NH_3{\cdot}H_2O$ was used as coprecipitation agent. If only $NH_3{\cdot}H_2O$ was used, pH value of the suspension may change in a large scale that will affect the reaction process greatly. It was related to not only the homogeneity of the powder but also the yield of NiO. These problems can be resolved to some extent using the buffer solution as coprecipitation agent. For NiO–YSZ system, there was still the problem of Ni^{2+} loss in $[Ni(NH_3)_4]^{2+}$ form. Yield of NiO can not be increased to a satisfactory level.

The quantity analysis results were shown in Table 2 in which NaOH was used as coprecipitation agent. Total yield of the powder was higher than 93%. No Ni^{2+} loss was observed in the form of $[Ni(NH_3)_4]^{2+}$. Both $Ni(OH)_2$ and $Zr(OH\ )_4$ can be entirely precipitated. NiO–YSZ powder can be accurately synthesized with NaOH as coprecipitation agent.

4. Conclusions

1. Nanometer NiO–ZrO_2 powder was synthesized by coprecipitation methods.
2. Cubic NiO and cubic ZrO_2 was obtained after calcinations at 600 °C. Powders calcined at different temperature showed different particle distribution.
3. When $NH_3{\cdot}H_2O$ was used as coprecipitation agent, a great deal of Ni^{2+} loss led to the deviation from the initial composition.
4. When $NH_3{\cdot}H_2O$–NH_4HCO_3 was used as coprecipitation agent, pH value can be better controlled and yield had been raised to some extant.
5. When NaOH used as coprecipitation agent, NiO–YSZ powder can be accurately synthesized by coprecipitation method.

References

[1] Y.H. Zhang, Y. Jiang, Z.G. Lu, Y.L. Dong, J.W. Yan, The effect of anode thickness in SOFCs with anode supported YSZ film, Electrochemistry 6 (2000) 285–290.

[2] S.H. Chen, K.A. Khor, Z.T. Xia, A complete polarization model of a solid oxide fuel cell and its sensitivity to the change of cell component thickness, Journal of Power Sources 93 (2001) 130–140.

[3] H. Yakabe, M. Hishinuma, M. Uratani, Y. Matsuzaki, I. Yasuda, Evaluation and modeling of performance of anode-supported solid oxide fuel cell, Journal of Power Sources 86 (2000) 423–431.

[4] J.W. Yan, Y.L. Dong, C.Y. Yu, Y. Jiang, Fabrication and characterization of anode substrates and supported electrolyte thin films for intermediate temperature solid oxide fuel cells, Journal of Inorganic Materials 16 (2001) 804–814.

[5] Y. Li, Z.L. Tang, Y.S. Xie, Z.T. Zhang, Preparation of Ni/YSZ for SOFC anodes by buffer-solution method, Materials Science and Technology 9 (2001) 91–94.

[6] K. Hideto, S. Yoshiyuki, Y. Toshihiko, M. Toshio, Properties of Ni-YSZ cermet as anode for SOFC, Solid State Ionics 132 (2000) 253–260.