

Journal of Alloys and Compounds 454 (2008) 447-453

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Characteristics of NiO-YSZ anode based on NiO particles synthesized by the precipitation method

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Received 24 August 2006; received in revised form 23 December 2006; accepted 29 December 2006 Available online 10 January 2007

Abstract

In order to increase the three phase boundary (TPB) length through lowering the NiO particles to submicro-size, NiO powder was synthesized by the precipitation method and the corresponding NiO-YSZ (8 mol% yttria-stabilized zirconia) composite anodes were investigated in this paper. The crystallite size of the as-synthesized NiO particle was 20–30 nm. The particles were agglomerated, but the agglomerates could be partially broken by grinding. The powder has an average particle size of $0.36 \,\mu$ m after grinding. NiO-YSZ anodes were fabricated by mixing the as-prepared NiO with commercial YSZ powders together. In order to form suitable porosity, flour was used as the pore-former, which played a key role in affecting the anode performance. Characteristics of the anodes, namely, shrinkage behavior, temperature-programmed reduction (TPR) measurement at a constant temperature (i.e., a modified TPR technique) and resistance characteristic during reduction were investigated. The maximum power density of the anode-supported YSZ film single cell was 905 mW/cm² at 750 °C based on the Anode-30 (NiO, YSZ and flour was mixed in the weight ratio of 5:5:3). As a summary, high cell performance could be achieved at reduced temperature with the as-fabricated NiO-YSZ anode containing a suitable microstructure.

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Keywords: SOFC; NiO; Precipitation method; NiO-YSZ anode; Porosity

1. Introduction

Solid oxide fuel cell (SOFC) has attracted numerous attentions over the past several decades due to their high-energy conversion efficiency, low pollution emission and high flexibility to various fuels [1]. Ni cermet is a widely used anode material for SOFC. Yttria-stabilized zirconia (YSZ) component is usually added to the cermet to form the composite anode, in order to extend the electrochemical reaction area from the anode/YSZ interface deep into the whole anode [2]. Furthermore, the functions of YSZ particles in the anode are to support the nickel-metal particles, inhibiting coarsening of the metallic particles at the fuel cell operating temperature, and provide an anode thermal expansion coefficient acceptably close to those of the other cell components [3].

The electrochemical activity of the anode drastically depends on a three-phase boundary (TPB) consisted of Ni grains, YSZ grains and fuel gases, where the electrochemical reaction occurs [4]. Therefore, it is essential to increase the TPB length in the anode. As for micro-sized NiO and YSZ powders, the TPB is fairly small due to the large Ni particle sizes in spite of using a large amount of Ni catalyst [5]. A large part of Ni surface apart from the contacting portions cannot contribute to the electrode reactions, resulting from the lack of O^{2-} ionic conductance [5]. It is thus desirable to reduce the Ni particle sizes to sub-micrometer or nanometer.

Nowadays, numerous methods have been proposed in the synthesis of NiO powder with reduced particle size, including homogeneous precipitation method [6], glycine-nitrate process (GNP) [7], sol-gel method [8], etc. The precipitation method

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^{0925-8388/\$ –} see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2006.12.130

[9,10] employed in our lab is an effective way to synthesize NiO powder with those sizes. The process is simple and easy to be controlled, does not need costly equipment, and thus is cost-effective. The single cell using the as-synthesized NiO-electrolyte composite anode exhibited high performances. For example, a single cell with a 12- μ m-thick Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) film on the NiO-SDC support yielded an extraordinary maximum power density of 1.08 W/cm² at 600 °C [9]. The good performance well demonstrates the superiority of this NiO. At the same time, few reports are concerned with the characteristics of the corresponding NiO-YSZ, such as sintering properties, electrical conductivities, temperature-programmed reduction (TPR) at a constant temperature, etc. Hence, concentration would be paid on these issues.

The fuels (H₂, CH₄, etc.) and products (H₂O, CO₂, etc.) of SOFC are diffusing through the cermet anode during operation, so containing a suitable porosity is very important, particularly for an anode-supported configuration with an anode of several hundred micrometers thick. Although the oxygen loss due to conversion of NiO to Ni can provide many micro-pores in the anode, it is still not sufficient for the diffusion of large amount of fuel and product through such a long thickness when the SOFC is operated at high current densities. As a consequence, many methods have been employed to produce additional porosity in the anode, e.g., pre-calcining the starting YSZ powder in the NiO-YSZ anode [11,12], adjusting the sintering process [13] and using organic pore-formers [14,15]. However, coarsening of the YSZ particles through pre-calcining would decrease the contacting portions of Ni and YSZ, and lower the TPB sites accordingly; along with increasing the anode porosity through lowering the sintering temperature, we have to confront the challenges associated with the decreasing conductivity due to poor particle-to-particle contact, the amplified anode overpotential due to the bad anode/electrolyte contact and the insufficiently densified electrolyte film for the anode-supported thin film SOFC. On the contrary, usage of a pore-former is an effective way to create the required porosity by adjusting the addition amount. High cell performance can still be obtained with the optimized anode microstructure [15,16]. So, flour is chosen in our study as a pore-former to acquire rational porosity.

In this paper, characteristics of the NiO powder synthesized by the precipitation method have been presented. The properties of the corresponding NiO-YSZ anodes are evaluated. Porosity effect is also taken into account as a key factor to the anode performance.

2. Experimental

2.1. NiO powder preparation and characterization

NiO particles were synthesized by the precipitation method [9]. Ni(NO₃)₂ 6H₂O (analytical reagent, A.R.) was dissolved by deionized water in the concentration of 0.5–1.0 mol/L. Ammonia (A.R.) solution was added to the stired solution drop by drop at room temperature. The molar ratio of Ni²⁺ ion to NH₃·H₂O was controlled at 1:2. The as-prepared deposition was aged at 70 °C for 4 h, and then washed by deionized water and ethanol in a centrifuge (TDL-5Z, Hunan Xingke, China), respectively. The resultant precipitation was subsequently dried at 105 °C, followed by calcining at 400 °C for 2 h to get pure nickel oxide powder.

The crystalline phase of the synthesized powder was examined by an X-ray diffractometer (XRD, Bede Scientific D¹), using Cu K α radiation ($\lambda = 0.15418$ nm). The grain size and morphology of the powder were taken by a transmission electron microscopy (TEM, JEOL JEM-1200EX). Particle size distribution of the powder was measured by a laser scattering technique (Mastersizer 2000, Malven Instruments), using deionized water as dispersant.

2.2. Characteristics of NiO-YSZ anodes

NiO, YSZ (TZ-8Y, Tosoh Corp., average particle size 0.2 μ m) and flour used as a pore-former were mixed in a weight ratio of 5:5:(1–3). The mixture was ground with a mortar and pestle by hand for 2 h to form the green anode powders. Anode powder without pore-former (NiO:YSZ=5:5) was also prepared.

For shrinkage behavior study, the as-formed powders were compacted into respective cylinders of 6 mm in diameter and 4–5 mm in length at 200 MPa. Shrinkage performances of the cylinders were tested from 50 to 1400 °C at a heating rate of 5 °C/min by a dilatometer (DIL 402C/3/G, Netzsch), using alumina sample holder, with air purge at a flow rate of 50 ml/min.

For the modified temperature-programmed reduction investigation, the aspressed pellets of 6 mm diameter were sintered at 1400 °C for 4 h, which was similar to the co-sintering process of the film/substrate bi-layers. The samples were about 0.5 mm thick and 40 mg in weight. The sintered pellets were then investigated with the conventional plug-flow reactor-TCD system (TPR, TP-5000, Tianjin Xianquan, China) to reveal reduction procedure of the anodes. Samples were heated to 700 °C at a constant heating rate of 10 K/min in the N₂ atmosphere with a flow rate of 50 ml/min. Subsequently, 5 ml/min H₂ was added at 700 °C. Although the feeding of the H₂ might cause small signal deviation from the baseline at the very moment, it seemed not to affect the qualitative analysis. Consumption of the H₂ due to the reduction of the NiO grains, was continually monitored by the TCD.

For DC electrical conductivity measurements, the as-formed anode powders were compacted into pellets with a diameter of 13 mm at 200 MPa, and sintered at 1400 °C for 4 h. The samples were then cut, and the dimensions of the measured pellets were 3.5 mm \times 2.0 mm \times 0.6 mm. The resulting anodes were measured with a four-probe method by a sourcemeter (Keithley 2400). N₂ gas with a flow rate of 50 ml/min was fed in the whole procedure and H₂ gas with a flow rate of 5 ml/min was supplied when the samples were under reduction at 700 °C.

Porosity of the samples was estimated according to the weight and dimensions. Microstructures of the fractured sintered anode pellets (1400 °C for 4 h) were characterized by a scanning electron microscope (SEM, S-570, Hitachi).

2.3. Single cell testing

The compacted anode pellets of 13 mm in diameter with a thickness of 0.6–0.7 mm were calcined at 1000 °C for 2 h to increase the mechanical strength. Dense YSZ films with a thickness of 15 μ m were fabricated by slurry spin coating, as described in our previous work [13,17]. Homogeneous electrolyte slurry consisting of YSZ powder and binders was coated on the anode substrates by repeating three consecutive coating-heating cycles. Finally, the bi-layers were co-fired at 1400 °C for 4 h to densify the electrolyte films. Sm_{0.2}Ce_{0.8}O_{1.9} (SDC)-impregnated La_{0.7}Sr_{0.3}MnO₃ (LSM) cathodes were subsequently coated on the YSZ films to form the single cells. The cells were tested with a four-probe method. 200 ml/min hydrogen as fuel was fed to the anode side and stationary air as oxidant at the cathode side. The anodes were reduced in situ at 700 °C. *I–V* characteristics were performed with an electrochemical interface (SI 1287, Solartron).

3. Results and discussion

3.1. Characteristics of NiO powder

According to the XRD pattern of the as-prepared NiO powder, a pure crystalline state of NiO with a cubic structure is observed. The average crystallite size of 23 nm is estimated from the Scherrer formula.



Fig. 1. TEM photograph of the NiO particles.

Fig. 1 presents TEM photograph of the powder. The particles show irregular shapes and have a size of 20–30 nm, which is in agreement with the estimated result from the XRD pattern. On the other hand, the particles seem to form severe agglomeration. The secondary particle sizes should be much bigger than the primary ones.

Laser scattering technique is used to reveal the secondary particle size distribution. Fig. 2 presents particle size distributions of three kinds of NiO powders (NiO-0, NiO-1 and NiO-2.5. For example, NiO-1 is denoted as the NiO powder ground with a mortar and pestle for 1 h) under different treating time. As for the green NiO-0, there are two peaks in the distribution curve, and the particle size is in the range of 0.13 and 2.4 μ m. The minimum particle size is one order of magnitude larger than that of the primary particles, corresponded to the agglomeration of the particle shown in Fig. 1. On the other hand, the aggregates could



Fig. 2. Particle size distributions of the NiO powders ground for different time.



Fig. 3. Sintering behavior of the different anodes.

be partially broken by the grinding treatment. Compared with the NiO-0, the first peak of NiO-1 is heightened and the second one lowered. NiO-1 has the average size of $0.36 \,\mu$ m, and 90 vol.% of the particles are less than $0.53 \,\mu$ m. The aggregates associated with the first peak are hard to be broken by the usual grinding or ultrasonic (20 kHz ultrasonic was applied during particle size measuring), while the soft aggregates corresponded to the second peak could be easily broken. Furthermore, note that the particle size distributions of NiO-1 and NiO-2.5 are quite similar. It indicates that most of the soft aggregates have been broken within 1 h, and any further grinding of the powder is of no help in reducing the particle size.

3.2. Characteristics of NiO-YSZ anodes

Fig. 3 shows sintering shrinkage behavior of the different anodes from 800 to 1400 °C. For simplicity, Anode-0, Anode-10, Anode-20 and Anode-30 are corresponded to the NiO-YSZ anode with 0, 10, 20 and 30 wt.% flour, respectively. As can be readily observed, the linear shrinkages are quite similar in the anodes in spite of the variation in the pore-former. Sintering shrinkage begins at 882, 874, 872 and 872 °C for Anode-0, Anode-10, Anode-20 and Anode-30, respectively. The more the pore-former, the lower the initial sintering temperature. Shrinkages of the four anodes are 15.5, 15.1, 14.7 and 15.4%, respectively. Although the shrinkages are quite similar for the different NiO-YSZ anodes, the porosity of the sintered samples is quite different since the initial densities of as-pressed pellets are quite different. The amount of porosity reserved in the anodes is still greater with more pore-former present, as shown in Table 1.

Fig. 4 presents shrinkage rate curves of the different NiO-YSZ anodes. For Anode-0, only one peak is observed, and the peak is higher than any other peaks in the curves of other anodes. It indicates that maybe only one sintering process or several sin-

Table 1 Porosity of different NiO-YSZ anodes

Sample	Anode-10	Anode-20	Anode-30
Porosity (%)	18	24	37



Fig. 4. Shrinkage rate curves of the different anodes.

tering mechanisms integrated in the peaks occurs in the anode within a wide temperature range. That should be related to the interaction of the NiO and YSZ grains during sintering and densification. For other curves, it is interesting to note that in principle, each curve has three peaks, as marked in the typical curve of Anode-10. According to the thermogravimetric analysis (TGA) result, the flour could be decomposed to gases before 500 °C at a heating rate of 5 °C/min in air, which is prior to the location of the peaks in the shrinkage rate curves (all higher than $1000 \,^{\circ}$ C). Therefore, the other two extra peaks should be associated with the pores in the anodes, which are created by the burnout of the additive pore-former. The pore size is 1.0-6.0 µm, as derived from the SEM photographs of the fractured NiO-YSZ anodes (sintered at 1400 °C for 4 h) with and without pore-former. The pores play a key role in affecting the sintering mechanisms in the anode. As can be seen, with more pore-former added, the first peak becomes more indistinct, the positions of the second and the third peaks are gradually reduced, and the third peak becomes clearer, wider and higher. Yan et al. [18] reported that the sintering could be divided into three stages with temperature. The first is the sintering within aggregates. The second is the surface diffusion and grain boundary diffusion. The last is the mass diffusion stage. In Anode-0, the three stages should subsequently take place within the peak at a wide range. Along with the addition of the pore-former in the anode, the aggregates would be covered by the fine flour particles. Then, the grain boundary among the aggregates should be different after burnout of the flour. One possible event is that the second sintering stage would bring forward, and gradually cover the effect of the first sintering stage in the shrinkage rate curve. The trend is more observable when more pore-former is added. The trend in the third peak shows larger densification rate and longer densification process with increased pore-former, which should be related to the variation in the number of pores per grain in the NiO-YSZ anodes. With respect to the SEM photographs, the number of pores in the sintered NiO-YSZ increases with the pore-former amount, as can also be observed in Fig. 7 In addition, the grain sizes of the anodes are quite similar. So, the number of pores per grain is ever larger with the increase in the pore-former. The result is consistent with the prediction by Zhao and Harmer [19] that increasing the number of



Fig. 5. Modified TPR profiles of the anodes at 700 °C.

pores per grain increased densification rate at the final stage of sintering.

Generally, the conventional TPR technique introduced in SOFC is used to detect the signal variety of the NiO-YSZ particle samples with the increase of the operating temperature at a reduced atmosphere. And the as-derived TPR profiles are usually employed to investigate the interaction between the NiO grains and YSZ grains [20,21]. In the present study, the modified TPR profile of the pellet anode was measured at a constant temperature, which is similar to the reduction process in a practical fuel cell operation. It is employed to evaluate the progress of the reduction process, as shown in Fig. 5. As can be seen in the curve, the signal increases rapidly in the first several minutes. After reaching a peak value, it gradually falls down to the baseline after several tens of minutes, which could be considered the end of the reduction. It can be readily seen that characteristics of the curves are largely affected by the amount of the pore-former. With the increasing pore-former in the samples, the trend is clear as follows:

- (a) The peak value is increased;
- (b) Slope of the signal, namely, the reduction rate is increased apparently in the first several minutes;

In the initial step, the reduction rate of the sample is primarily determined by the surface area (i.e., the sample exposed outside and the open pores inside), which is increased with the increasing porosity. Sufficiency in the surface area would be helpful for diffusion of the mixed gases to the reaction region. The rapid increase in signal is due to rapid consumption of the H₂ gas by the sufficient exposure of the NiO particles. This is the reason why the reduction rate in the initial stage is increased with more porosity. Furthermore, the sufficient exposure of the NiO for reaction would consequently result in the increasing peak value. After the terminated reduction of the NiO in the surface, the reaction beneath the surface continues to carry out. Whereas, the reduction rate is then controlled by the diffusion rate of the gas in the micro-pores generated by the NiO reduction, which becomes much slower. This, in turn, causes the decreasing H₂ assumption, and leads to the gradual descending TPR signal. High porosity means more H₂ pathway into the sample



Fig. 6. Resistance characteristic of Anode-20 (3.5 mm \times 2.0 \times 0.6 mm) before and after reduction.

and less diffusion depth, resulting in faster termination of the reduction.

Fig. 6 describes the resistance characteristic of Anode-20 $(3.5 \text{ mm} \times 2.0 \text{ mm} \times 0.6 \text{ mm})$ before and after reduction. Before reduction, the resistance decreases with temperature mainly due to the increasing ionic conductivity of the connected YSZ matrix in the anode. At the moment of feeding H₂ flow, the resistance decreases immediately for about three orders of magnitude, indicating reduction of the NiO to Ni in the surface area of the sample in a short time. It is in agreement of the TPR profile in the initial stage. The reduction continues to carry out from the surface to the inner of the samples with the operating time, resulting in the decrease of the resistance continuously. After reduction for 10 min, the resistance comes to a minimum. It should not be regarded as the end of the reduction process; otherwise it would be inconsistent with the TPR result (the reduction is terminated within \sim 35 min, and the two samples have a similar thickness). It was reported that Ni particles easily shrink to larger particles during reduction and caused disconnection of the Ni particles, which would lead to decrease in the conductivity [3,22]. Therefore, two processes, namely, decrease of resistance due to the reduction of NiO to Ni and increase of the resistance due to shrinkage of the Ni particles would affect the resistance of the sample simultaneously. In the initial reduction stage, the effect of fast conversion of NiO to Ni suppresses the effect of the shrinkage of Ni particles, resulting in rapid decrease of the resistance. At 10 min, a critical state between the effect of NiO reduction on the decrease of the resistance and the effect of Ni shrinkage on the increase of the resistance is reached. It leads to the minimum sample resistance. Thereafter, the effect of the interaction converses since the reduction rate becomes lower and lower with the operating time. According to the TPR result, the reduction of NiO to Ni completes in 35 min. In other words, the effect of Ni shrinkage dominates the resistance variation after 35 min. A steady state would be achieved eventually when the Ni particle shrinkage comes to an end. As also can be seen in Fig. 6, the resistance is gradually decreased when the temperature is decreased, which shows the similarity of the conducting performance with the metal due to continuous nickel distribution in the YSZ matrix. Resistance characteristics of the other anodes are similar to that of Anode-20. Table 2 compiles maximum conductivities of the anodes at 700 °C during reduction.

Table 2

Maximum conductivities of the Ni-YSZ anodes after reduction at 700 °C

Sample	Anode-10	Anode-20	Anode-30
Maximum conductivity (S/cm)	837	599	554

It is clear that the conductivity decreases with the increased pore-former amount. The pores occupy the locations where there otherwise would have been nickel particles to provide electrical connection, and in turn lowers the electrical conductivity. Anyhow, the conductivities of the reduced Ni-YSZ samples all meet the requirement of the anodes for SOFC.

Fig. 7 shows the microstructure of the fractured Ni-YSZ anodes after reduction. Before reduction, the anodes were sintered at 1400 °C for 4 h. The porosity of the NiO-YSZ samples is shown in Table 1. Assuming no volume change in the anode occurs during the reduction, an additional porosity of 19% would be produced after reduction. As can be seen in Fig. 7a, the particles and pores are uniformly distributed. The particles appear to contact well with each other, and the average particle size is less than 1.0 μ m. The pores (less than 1.5 μ m) in Anode-0 should be originated from two ways. They are the pores left in the sample due to incomplete densification and oxygen loss along with the conversion of NiO to Ni during reduction. To some extent, the uniformly distributed fine grain and pores would result in the sufficient TPB length. However, the diffusion of gases within such anode would be relatively slow and thus limit the overall reaction rate [15]. So, some additional pores should be added. Compared with the morphology in Fig. 7a, the larger pores in other Ni-YSZ anodes should be created by the burnout of the organic pore-former. And the amount of the big pores increases when more pore-former is added. Presence of the pores, particularly large pores would be beneficial for the transport of fuel gas and diffusion of the exhaust gas and therefore promote the reaction rate. On the other hand, the increasing amount of the big pore would consequently decrease the TPB density in the anode. Therefore, the amount of the pore-former utilized should be optimized to achieve a desirable cell performance.

3.3. Electrochemical performance of the fuel cells

Electrochemical characteristics of the cells based on the various anode supports at 750 °C are presented in Fig. 8. Since the YSZ film and the cathode layer were fabricated through the same process, the difference in the cell performance should be due to the different anode microstructures. The cell, e.g., Cell-10, corresponds to the single cell based on Anode-10. The open-circuit voltages (OCV) of the cells are all higher than 1.0 V, indicating the YSZ films are fully dense. It should be due to good matching of the NiO-YSZ anode/YSZ film bi-layers during co-sintering. Maximum power densities (MPD) of Cell-10, Cell-20 and Cell-30 are 371, 785 and 905 mW/cm², respectively. Haslam et al. [15] reported that cell performance was the greatest when an optimum was achieved. It is related to an equilibrium between the adequate gas transport to the TPB and loss of the TPB due to the increasing porosity. It is clear that the enhancement in gas



Fig. 7. Microstructures of the Ni-YSZ anodes after reduction: (a) Anode-0, (b) Anode-10, (c) Anode-20 and (d) Anode-30.

transport would bring about the loss of TPB. However, the final effect on the cell performance would depend on the predominant process. It can be seen that the performance of Cell-10 is relatively low. It should be attributed to the low anode poros-



Fig. 8. I-V and I-P characteristics of the cells based on various anode supports.

ity (\sim 37%), preventing the fast gas transport to the reaction zone and limit the overall reaction rate. It is reported that the negative curvature in the I-V curve usually related to the concentration polarization [23]. However, this curvature is not clearly discernible in the high current density region concerning the I-Vcurve of Cell-10. It is probably due to the relatively low cell output and the excess supply of fuel gas (200 ml/min H₂). Anyhow, the gas transportation property is considerably improved when more porosity is created in the anode, e.g., Anode-20. Due to the improved gas transport property, the cell performance is largely enhanced for Cell-20, which is increased by 112% compared with that of Cell-10. The cell performance is further promoted when Anode-30 is used. This considerable enhancement well demonstrates the importance of anode microstructure in affecting the cell performance. At the same time, it should be noted that the increase in the MPD of Cell-30 is only 15% compared with that of Cell-20. It is much lower than the considerable promotion from Cell-10 to Cell-20. The effect of TPB loss process becomes more and more remarkable. As can be expected, optimum amount of the pore-former is around 30 wt.%. A detailed investigation should be carried out in the future.

4. Conclusions

NiO powder with submicron-sized particles was synthesized by the precipitation method. Investigation showed that the Ni-YSZ anodes with different porosity met the requirements of SOFC. The porosity affected the anode performance drastically. The best performance of the anode-supported YSZ film single cell was 905 mW/cm² at 750 °C based on the Anode-30. The optimum amount of the pore-former related to the optimized cell performance was considered around 30 wt.%, i.e., YSZ, NiO and flour were mixed in the weight ratio of 5:5:3. As a summary, with the as-prepared Ni-YSZ cermet containing a suitable microstructure, high cell performance could be achieved at reduced temperatures.

Acknowledgements

The authors gratefully acknowledge financial supports from the Ministry of Science and Technology of China under contract no. 2001AA323090.

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