

Short communication

# Synthesis and characterizations of composite particles for solid oxide fuel cell anodes by spray pyrolysis and intermediate temperature cell performance<sup>☆</sup>

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## Abstract

NiO–Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC) composite particles were synthesized using starting solutions containing the components for NiO–SDC and various amounts of nitric acid. It was found that the particles had a different surface morphology and specific surface area depending on the pH values of the starting solutions. SOFC single cell using the composite particles as an anode electrode was examined at an intermediate temperature to clarify the relationship between particle morphology and cell performance. High and consistent cell performance was obtained when the composite particles were synthesized using the solutions containing large amounts of nitric acid. It was considered that the morphology and the specific surface area of NiO–SDC composite particles played an important role realizing a high cell performance anode.

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## 1. Introduction

The operation of solid oxide fuel cells (SOFCs) at intermediate temperatures between 600 °C and 800 °C provides several advantages (i.e. extensive selection of low-cost and high-performance component materials, high flexibility of SOFC structure, etc.). Since lowering the operation temperature increases not only the ohmic loss but also the polarization loss at the anode and the cathode, it is necessary to develop highly active electrodes that show sufficiently low polarizations at intermediate temperatures. We have developed a Ni–Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> (SDC) cermet anode that shows high cell performance at temperatures below 800 °C, by using highly dispersed NiO–SDC composite particles synthesized by a

spray pyrolysis method [1–3]. The synthetic conditions of the NiO–SDC composite particles, however, should be investigated further to realize the optimized anode properties. It was reported that the presence of additional anion species in the starting solutions for spray pyrolysis had significant influence on the properties of the particles [4,5]. In this paper, we investigate the effects of nitric acids added to the starting solution for spray pyrolysis on the properties of NiO–SDC composite particles. And, we describe the relationship between the properties of various NiO–SDC composite particles and the cell performance using these particles for the anode electrode.

## 2. Experimental

### 2.1. Synthesis of NiO–SDC composite particles by spray pyrolysis method

NiO–SDC composite particles were synthesized by spray pyrolysis method as shown schematically in Fig. 1. Aque-

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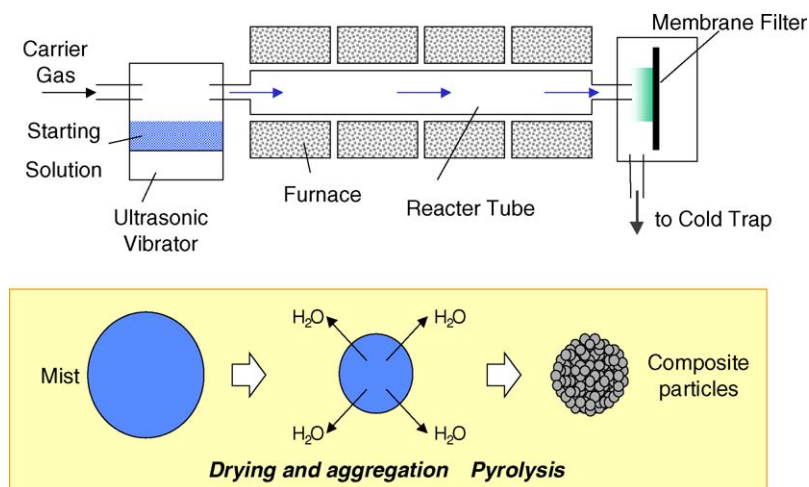


Fig. 1. Synthesis of composite particles by spray pyrolysis.

ous starting solutions containing the desired composition of corresponding cations were prepared by dissolving nickel acetate, cerium nitrate, samarium nitrate and various amounts of nitric acid (60 mass%) in the 500 ml starting solutions. These solutions were atomized with an ultrasonic vibrator operating at 1.65 MHz. The droplets were transported into a reaction furnace using air as a carrier gas at a fixed flow rate of  $1 \text{ dm}^3 \text{ min}^{-1}$ . The reaction furnace consisted of four independent heating zones, of which temperatures were set at  $200^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $800^\circ\text{C}$  and  $1000^\circ\text{C}$ , respectively. The NiO–SDC particles were collected using a membrane filter.

### 2.2. Characterization of NiO–SDC composite particles by spray pyrolysis method

X-ray diffraction (XRD, Shimadzu XRD-6000) analysis was carried out to confirm that the composite particles possessed the individual NiO and SDC crystal structures. Specific surface area of the NiO–SDC composite particles was measured by means of specific surface analyzer (YUASA-IONICS NOVA 2000). The microstructure of the particles was observed by scanning electron microscope (SEM, Hitachi S-2380N). The pH values of the solutions were measured with a pH meter (YOKOGAWA Model PH82) at room temperature. The pH values of the solutions were constant during the spray pyrolysis.

### 2.3. Cell fabrication process

For the electrolyte, we selected a lanthanum gallate-based electrolyte, which possesses high oxide ion conductivity [6–8]. Commercially available oxide powders ( $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{CoO}$ ) were proportionally mixed, ball-milled and calcined in air to obtain the LSGMC powder with the chemical formula of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_{3-\delta}$ . The product of the calcination process was re-ground and mixed with an organic

binder to be tape-casted into green sheet. Disks were then cut out and sintered in air at  $1400\text{--}1500^\circ\text{C}$  for 6 h to obtain a  $200 \mu\text{m}$  thick LSGMC electrolyte with relative density greater than 98%.

For the anode, the slurry containing the NiO–SDC composite particles was screen-printed onto the electrolyte, so as to give an effective electrode area of  $2 \text{ cm}^2$ , and then fired in air at  $1280^\circ\text{C}$  for 3 h.

For the cathode, we selected samarium cobaltite compounds, which have been demonstrated to show very small polarization [9]. The slurry made of  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (SSC) powder was screen-printed onto the electrolyte to give the same effective electrode area of  $2 \text{ cm}^2$ . The final sintering was performed in air at a temperature of  $1100^\circ\text{C}$  for 3 h to obtain the porous cathode.

### 2.4. Single cell performance test

The single cell tests were carried out at  $750^\circ\text{C}$ . Air was used as an oxidant ( $31 \text{ ml min}^{-1}$ ), and dry hydrogen gas was used as a fuel ( $7.9 \text{ ml min}^{-1}$ ) (Fig. 2). NiO in the anode was reduced to Ni under the fuel atmosphere prior to measuring the power generation characteristics. For the electrochemical characterization, the current-interruption technique was

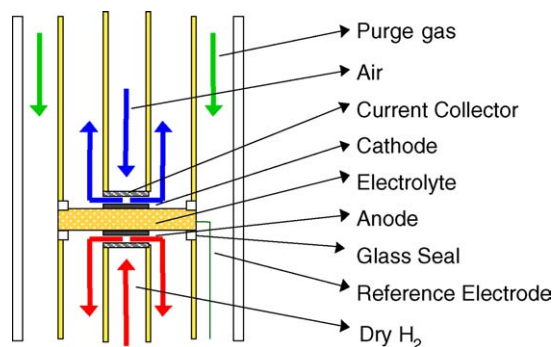


Fig. 2. Schematic view of testing apparatus for Ni–SDC/LSGMC/SSC.

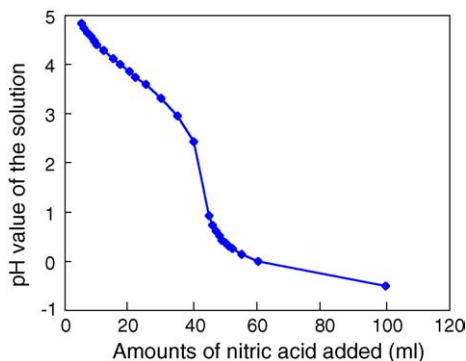


Fig. 3. The relationship between pH values of the starting solutions and the amounts of nitric acid in the starting solutions for spray pyrolysis.

applied to measure the IR drop and the polarization loss at the electrode. As a reference electrode, Pt wire was wound around the LSGMC pellet and fixed with platinum paste.

### 3. Results and discussion

#### 3.1. Characteristics of NiO–SDC composite particles synthesized by spray pyrolysis method

NiO–SDC composite particles were synthesized using the starting solutions containing the components for NiO–SDC and various amounts of nitric acid.

Fig. 3 shows the relationship between the pH values of the solutions and the amounts of nitric acid in the starting solutions for spray pyrolysis of NiO–SDC. The pH value was steeply decreased by adding 50 ml nitric acid, because dissociation of nickel acetate with nitric acid is completed and the pH starts to be controlled by the excess amount of nitric acid. Fig. 4 shows the relationship between the specific surface area and the pH values of the solutions. The solutions that

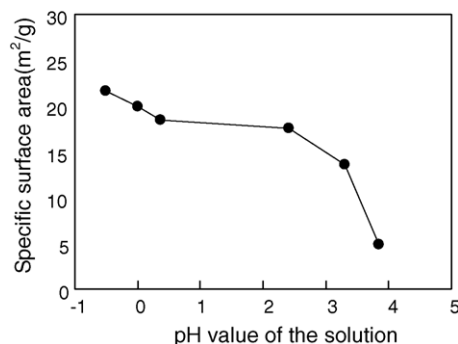


Fig. 4. The relationship between the specific surface area and pH values of the starting solutions for spray pyrolysis of NiO–SDC.

were in the low pH range with large amounts of nitric acid produced the particles that had large specific surface area. On the other hand, the solutions that were in the relatively high pH range with small amounts of nitric acid gave the particles that had small specific surface area. It was considered that the particles had different specific surface area and surface morphology depending on the pH values of the starting solutions.

Fig. 5 shows SEM images of NiO–SDC composite particles with various amounts of nitric acid in the starting solutions for spray pyrolysis. It was found that the particles had different surface morphology depending on the pH values of the starting solutions. The solutions which were in the low pH range with large amounts of nitric acid (50 ml, 60 ml and 100 ml) in the total amounts of 500 ml produced the particles, which had smooth surface. On the other hand, the starting solutions, which were in the relatively high pH range, with small amounts of nitric acid (20 ml, 30 ml and 40 ml) gave the particles, which had rather rough surface with some dimples. The rough surface and dimples did not lead to high specific surface area, whereas the smooth surface area, which

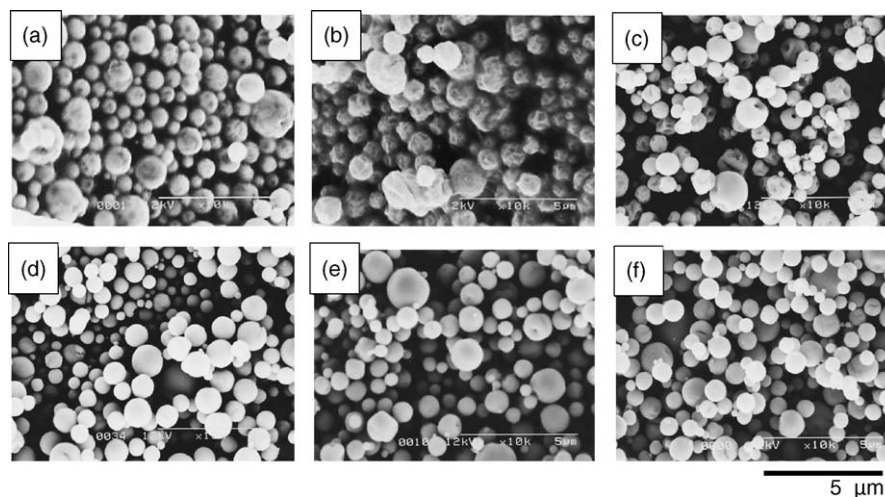


Fig. 5. SEM images of NiO–SDC composite particles synthesized by spray pyrolysis with various amounts of nitric acid – (a) 20 ml, (b) 30 ml, (c) 40 ml, (d) 50 ml, (e) 60 ml and (f) 100 ml – in the starting solutions.

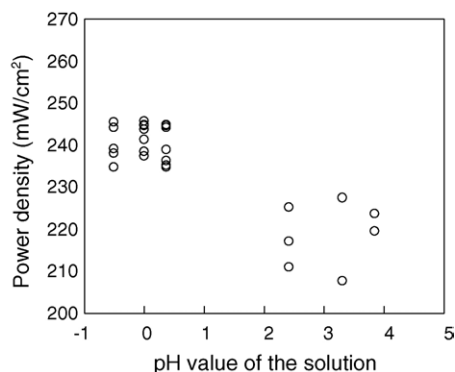


Fig. 6. The relationship between SOFC power density ( $0.3 \text{ A cm}^{-2}$ ,  $750^\circ\text{C}$ ) and pH values of the starting solutions for spray pyrolysis of NiO–SDC.

was observed by SEM, had a wealth of pores. Therefore, the collapse of pores in the smooth surface would result in the rough surface and dimples.

It was expected that these differences of the property of NiO–SDC composite particles would give an impact on the power density of SOFC single cell whose anode was made by them.

### 3.2. Single cell performance test

Fig. 6 shows the variation of SOFC power density (at  $0.3 \text{ A cm}^{-2}$ ,  $750^\circ\text{C}$ ) with the pH values of the solutions. Fig. 7 shows the voltage loss of SOFC due to the IR drop and both anodic and cathodic polarizations ( $\eta_a$  and  $\eta_c$ ). Several cells were tested to confirm the reproducibility. The use of particles synthesized with the solutions in the low pH range ( $<0.4$ ) led to show high performance with small deviation, whereas the use of particles synthesized with the solutions in the relatively high pH range ( $>2.4$ ) led to show low performance with large deviation. This behavior is considered to be related to the difference of the specific surface area and the surface morphology of NiO–SDC composite particles depending on the pH values of the starting solutions.

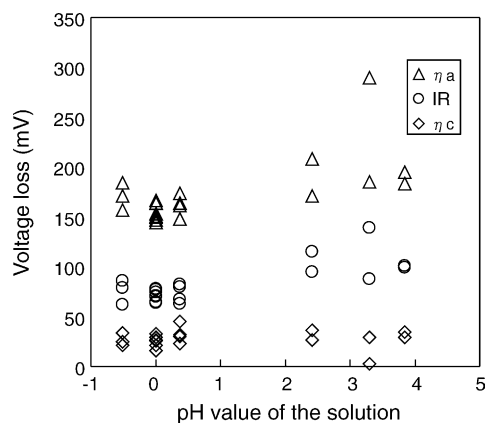


Fig. 7. The relationship between the voltage loss of SOFC (IR: ohmic loss,  $\eta_a$ : anodic polarization and  $\eta_c$ : cathodic polarization) with  $0.3 \text{ A cm}^{-2}$  at  $750^\circ\text{C}$  and pH values of the starting solutions for spray pyrolysis of NiO–SDC.

The difference in the pH value due to the amounts of nitric acid gives different environment near the cations (Ni, Ce and Sm). There are two kinds of anions in the starting solution. One is a nitrate ion and the other is an acetate ion. In the relatively high pH range with small amounts of nitric acid added, acetate ions work as counter ions of the cations and are present close to cations. During the drying of the droplets and the aggregation process of particles, the acetate ions may react with air exothermically. This rapid change is considered to make the resulting particles rather rough surface and small specific surface area. On the other hand, in the low pH range with large amounts of nitric acid added, acetate ions tend to exist far from cations and nitrate ions are associated with cations instead, which give rather moderate reaction during the period of the spray pyrolysis, because the endothermic decomposition of nitrate ions occurs at slower rates. This process generates the particles having smooth surface with large specific area, which can give the anode fine network structure of Ni and SDC when they are sintered on the electrolyte. The high and reproducible cell performance was obtained with the anodes having fine network structure by sintering the NiO–SDC composite particles synthesized with the solutions, which were in the low pH range ( $<0.4$ ).

## 4. Conclusions

NiO–SDC composite particles were synthesized by the spray pyrolysis method using starting solutions containing the components for NiO–SDC and various amounts of nitric acid. It was found that the particles had different surface morphology and the specific surface area depending on the pH values of the starting solutions and that the particles synthesized with the solutions which were in the low pH range gave high and reproducible SOFC performance. It is considered that the morphology and the specific surface area of NiO–SDC composite particles play an important role of realizing a high cell performance anode.

## References

- [1] S. Ohara, R. Maric, X. Zhang, K. Mukai, H. Yoshida, T. Inagaki, K. Miura, T. Fukui, J. Power Sources 86 (2000) 455.
- [2] T. Inagaki, H. Yoshida, K. Miura, S. Ohara, R. Maric, X. Zhang, K. Mukai, T. Fukui, SOFC-VII (Electrochem. Soc. Proc.) 16 (2001) 963.
- [3] T. Fukui, S. Ohara, K. Murata, H. Yoshida, K. Miura, T. Inagaki, J. Power Sources 106 (2002) 142.
- [4] K.H. Kim, S.Y. Choi, Y.C. Kang, C.H. Kim, H.D. Park, J. Korean Ceram. Soc. 38 (1998) 173.
- [5] Y. Itoh, K. Okuyama, J. Ceram. Soc. Jpn. 111 (2003) 815.
- [6] T. Ishihara, H. Matsuda, Y. Takita, J. Am. Chem. Soc. 116 (1984) 3801.
- [7] T. Ishihara, T. Akbay, H. Furutani, Y. Takita, Solid State Ionics 113–115 (1998) 585.
- [8] T. Ishihara, T. Shibayama, M. Honda, H. Furutani, Y. Takita, Abstracts for 1998 Fuel Cell Seminar, CA, USA, 1998, p. 104.
- [9] T. Ishihara, M. Honda, T. Shibayama, H. Minami, H. Nishiguchi, Y. Takita, J. Electrochem. Soc. 145 (1998) 3177.