

Title	Synthesis of Ceramics Composite Nanoparticles by Spray Pyrolysis
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Citation	Transactions of JWRI. 2007, 36(2), p. 99-101
Version Type	VoR
URL	https://doi.org/10.18910/11461
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Synthesis of Ceramics Composite Nanoparticles by Spray Pyrolysis[†]

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KEY WORDS: (NiO-SDC) (Composite) (Nanoparticles) (Spray Pyrolysis)

1. Introduction

Spray pyrolysis (SP) is a powder synthesis method which enables spherical powders to be prepared through the following steps^{1,2}: (1) solution droplet formation using an aerosol generator, (2) solvent evaporation and solute precipitation near the reactor entrance, (3) decomposition of solute to form ceramics powder at higher temperatures and (4) sintering. The advantage of the SP technique compared with other wet chemical processes is that the solution is divided into micron-sized droplets in which both chemical and physical reactions are driven to completion, providing unique control over the thermal decomposition and sintering stages of inorganic powder formation. It is therefore possible to control the morphology and composition of the powders by controlling synthesis conditions and the intra-droplet-powder reactions.

In order to make efficient solid oxide fuel cell (SOFC), we have been using nanosized NiO-(CeO₂)_{0.8}(SmO_{1.5})_{0.2} (NiO-SDC) composite particles prepared by SP to form anodes for low temperature operation (600-800 °C)³⁻⁵. For optimum SOFC performance, electrodes must exhibit good lateral conductivity, electrochemical activity, and chemical stability towards the electrolyte and gas environments. These factors depend on the composition and microstructure of the electrode, which is determined by the nature of the starting powder and the fabrication method. In our previous studies, we reported the importance of microstructure control to obtain high performance cermet anodes when we used Ni as a catalyst³⁻⁵. In this brief paper, we report the synthesis of NiO-SDC composite nanoparticles with closely controlled particle size, morphology and composition for use in SOFC anodes.

2. Experimental

Four NiO-SDC composite nanoparticles with different NiO contents were synthesized by SP. The SP system employed was similar to that used previously².

NiO-SDC composite nanoparticles were obtained from solution, which was prepared from Ce(NO₃)₃·7.5H₂O, Sm₂O₃ and Ni(CH₃COO)₂·4H₂O. This initial solution was atomized with an ultrasonic vibrator operated at 1.7 MHz. Droplets were transported to a reaction furnace using air as a carrier gas with a fixed flow rate of 0.5 L/min. The reactor consisted of three independent heating zones. The temperatures of heating zones 1, 2 and 3 were set to 300, 600 and 900°C, respectively. The composite nanoparticles from the furnace outlet were collected using an organic filter. After SP, all composite nanoparticles were calcinated at a temperature of 1000°C for several hours.

The composition of synthesized nanoparticles was evaluated by X-ray fluorescence analysis. The particle size distribution of the nanoparticles was measured by laser diffraction and scattering. The morphology of the nanoparticles was examined by scanning electron microscopy (SEM) with an energy dispersive spectrometer (EDS).

3. Results and Discussion

Table 1 shows the solution concentration, composition and mean particle size for four kinds of NiO-SDC composite nanoparticles obtained from solution with different NiO contents by the SP technique. For each starting composition, the NiO content of the composite nanoparticle obtained is almost the same as the NiO content of the starting solution. These results clearly show that it is possible to obtain excellent control of the chemical composition of the composite nanoparticle using SP. **Figure 1** shows the particle morphologies of composite nanoparticles obtained by SP from different starting solution concentrations. It is clear from this figure that spherical composite nanoparticles were formed for both concentrations. From EDS, we also determined that the composition was uniform throughout the composite nanoparticles. As the solution concentration increases, it can be seen that the particle size also increases and a larger fraction of smaller composite nanoparticles is formed at the lower solution

[†] Received on December 14, 2007

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Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

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Table 1 Characterization of NiO-SDC composite particles by spray pyrolysis.

Solution Concentration (mol/L)	NiO content in starting solution (wt.%)	NiO content in composite nanoparticle (wt.%)	Mean particle size (nm)
0.15	15	16	500
0.25	40	40	600
0.45	60	59	900
0.45	70	68	900

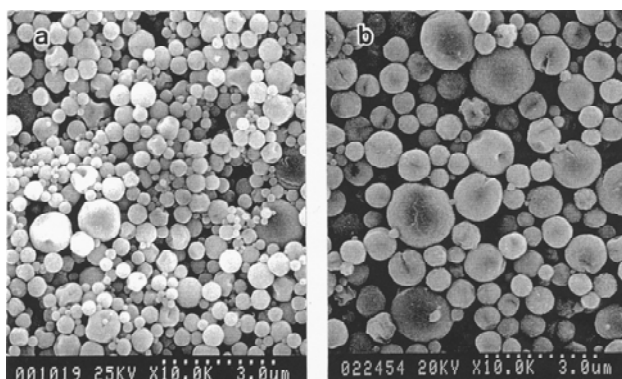


Fig. 1 SEM micrographs of NiO-SDC composite nanoparticles formed from different starting solution concentrations of (a) 0.15 mol/L and (b) 0.45 mol/L.

concentration of 0.15 mol/L, Fig. 1a.

The crystallite sizes of composite nanoparticles obtained by SP have been calculated from X-ray diffraction peak broadening using the Scherrer formula. For all starting solutions, the crystallite size was almost the same, e.g., for both NiO and SDC, it was about 15 nm (see **Table 2**). During the calcination process, there is no significant change in particle size (**Fig. 2**). However, the crystallite size of the NiO in 68 wt.% NiO composite nanoparticles is significantly larger compared to that of NiO in 16 wt.% NiO composite nanoparticles. As can be seen in Table II, both the NiO and SDC crystallite sizes increased during crystallization at 1000°C, and the crystallites of NiO are significantly larger than those of SDC. The change in crystallite size with heating can be explained as follows: The composite nanoparticles obtained after SP at 1000°C were spherical with smooth surfaces due to the lack of crystallization during synthesis.

During calcination at 1000°C for 24 h, crystallization occurs along with partial sintering of the crystallites inside the composite nanoparticles. The distribution of the NiO and SDC crystallites inside the composite nanoparticles is dependent on the amount of NiO in the starting solution. For the 15 wt.% NiO starting solution, the composite nanoparticle after SP is composed of grains of NiO and SDC randomly distributed inside the particle. There is no direct contact between NiO crystallites and therefore no sintering between NiO

Table 2 Crystalline sizes of NiO and SDC before and after calcinations calculated by the Scherrer formula from XRD patterns.

Before calcination		After calcination	
NiO (nm)	SDC (nm)	NiO (nm)	SDC (nm)
15	14	40	30
15	14	60	40
15	14	100	50
15	14	100	50

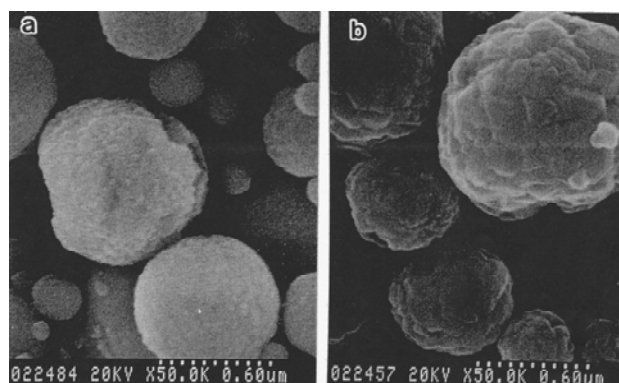


Fig. 2 SEM micrographs of NiO-SDC composite nanoparticles after calcinations with different NiO contents (a) 16 wt. % and (b) 68 wt. %

crystallites inside of the composite nanoparticles during calcinations. In contrast, when the concentration of NiO in the starting solution is 70 wt.%, the NiO crystallites form the outer shell (as shown in Fig. 2b) of the composite nanoparticle with a small quantity of SDC grains, with most of the SDC grains in the core of the particle. This kind of distribution results in many contacts between NiO grains on the surface of the composite nanoparticles, and the consequent crystallization and sintering between NiO crystallites leads to an increase in crystallite size during calcinations (Table II). We believe that this kind of crystallite distribution plays an important role in the microstructure formation of the anode during sintering, with elongated NiO grains well connected and SDC grains dispersed on the surface of NiO grains.

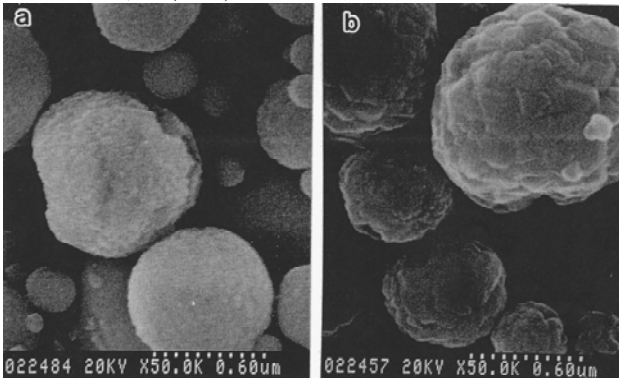
4. Conclusion

In conclusion, we have successfully synthesized NiO-SDC composite nanoparticles with controlled particle size, morphology and different NiO contents by the SP technique.

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