

Colloidal spray pyrolysis preparation and characterization of nanocrystalline NiO-SDC composite powders for SOFCs

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Abstract The nanocrystalline NiO-Ce_{0.8}Sm_{0.2}O_{1.9} (NiO-SDC) composite powders were prepared by colloidal spray pyrolysis. The morphological characteristics, particle size and distribution of the particles obtained from calcining spray pyrolysis derived powders were investigated. The results showed that: The composite powders from spray colloidal solutions with Ni hydroxy carbonate sols were better than those with Ce-Sm hydroxy carbonate sols in crystallinity and primary particle size. The powders had a very narrow particle size distribution centered at 250 nm in which NiO and SDC primary particles were distributed homogeneously. The composite powders could favor the formation of high performance anodes of SOFCs.

Keywords Nanocrystalline powder ·
Colloidal spray pyrolysis · NiO-SDC · SOFC

1 Introduction

Solid oxide fuel cells (SOFCs) as a new technology for electrical power generation attract great attention [1, 2]. As an effective anode material, Ni-Ce_{0.8}Sm_{0.2}O_{1.9} (Ni-SDC) cermet can make SOFCs operate in low temperature, and result in electrolyte with small polarization and ohmic loss [3]. High performances of SOFCs require Ni-SDC cermet to have a desired microstructure with nanocrystalline grains and homogeneous distributions of Ni and SDC. Nano-

crystalline phases can greatly increase the places where catalytic and electrochemical reactions take place, homogeneous distribution of the two phases causes the reactions to co-occur easily, which is necessary for anode operation.

However, the formation of the desired microstructure depends on many factors. Among them, the character of the starting powders is a more crucial factor. Only the starting NiO-SDC powders have nanocrystalline grains and homogeneous distributions of NiO and SDC, which is possible to obtain the desired Ni-SDC cermet anode. Considering ceramic processing technology, it also requires the starting powders have a narrow particle size distribution.

Spray pyrolysis is one of effective techniques for preparing particles on a large scale [4, 5]. However, spray pyrolysis derived powders often have a little segregation between two phases. The problem can be solved if spray solution is replaced by colloidal solution, the colloidal spray pyrolysis technique also increase productivity [6].

In this paper, the nanocrystalline NiO-SDC composite powders were prepared by colloidal spray pyrolysis technique, trying to obtain good starting powders for the preparation of Ni-SDC cermet anode. The morphology, microstructure and particle size distribution of the resulting powders were characterized and discussed.

2 Experimental

2.1 Preparation of NiO-SDC composite powders

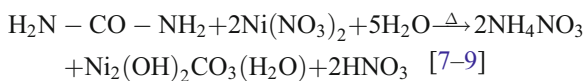
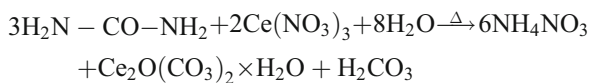
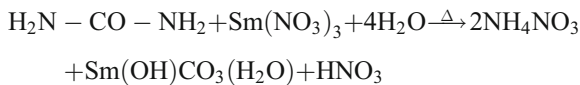
A mixed solution of Ce(NO₃)₃ (≥99.95%) and Sm(NO₃)₃ (≥99.95%) with Ce³⁺/Sm³⁺ molar ratio of 4/1 was prepared. For the preparation of sols, appropriate amount of H₂NCONH₂ (≥99.0%) was added into the mixed solutions, then the solution warmed at 85 °C for 2 h to form Sm(OH)

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Table 1 Preparation conditions of spray colloidal solution.

Series	Spray colloidal solution				
	Sol	Solution		The resulting NiO-SDC composite powders to label as	
A	Ce-Sm hydroxy carbonate sol	100 ml×0.04 M	Ni nitrate solution	100 ml×0.064 M	Sample A1
		100 ml×0.16 M		100 ml×0.256 M	Sample A2
		100 ml×0.32 M		100 ml×0.512 M	Sample A3
B	Ni hydroxy carbonate sol	100 ml×0.064 M	Ce-Sm nitrate solution	100 ml×0.04 M	Sample B1
		100 ml×0.256 M		100 ml×0.16 M	Sample B2
		100 ml×0.512 M		100 ml×0.32 M	Sample B3

CO₃ and Ce₂O(CO₃)₂ sol [7]. A Ni(NO₃)₂ (≥98.0%) solution was prepared. Same amount of H₂NCONH₂ was added into the solutions, then warmed at 90 °C for 3.5 h to form Ni₂(OH)₂CO₃ sol [8]. The chemical equations of the above reactions are given:



Two series of spray colloidal solutions were prepared using the above solutions and sols. The specific preparation conditions of mixing solution and sol are listed in Table 1.

For preparation of NiO-SDC composite powders, a micro airflow spray drier (WPG, Jiangyin drier machine factory) was adopted. The spray temperature of 400 °C, the flow rate of spray colloidal solutions of 2.5 ml/min and the spray air pressure of 0.4 MPa were used. The spray pyrolysis derived powders were then calcined at 750 °C for 2 h to form the NiO-SDC composite powders.

2.2 Characterization of NiO-SDC composite particles

X-ray diffraction (XRD, Model D/MAX-RA, RIGAKU) using Cu K_α radiation was applied to characterize crystalline phases of the composite powders. Data were collected in the range of 10–80°, 2θ, in steps of 0.04° for 1 s per step. Transmission electron microscopy (TEM, Model JEM-00CX, JEOL Co.) was used to observe the morphology of the powders. The particle size distribution of the composite powders was measured in Malvern Zeta-Sizer (Nano-S90, Malvern).

3 Results

XRD patterns (Fig. 1) of the 750 °C calcined powders from two series show that these powders have two crystalline phases of cubic NiO and cubic SDC, and are composite powders. However, the NiO phase in the powders from series A is developed much better than that from series B.

The primary particle size of the NiO-SDC composite powders slightly increases with the concentration of spray colloidal solutions as shown in Fig. 2. The size for each sample is listed in Table 2. It can be seen that the NiO-SDC composite powders prepared from Series B have a smaller size than those from series A.

The SAED pattern (Fig. 3) of an agglomerated particle [Fig. 2(f)] in NiO-SDC composite powders from series B shows to have two phases of NiO and SDC.

Figure 4 shows the particle size distribution of NiO-SDC composite powders from series B, the size distribution is very narrow and centered at 250 nm.

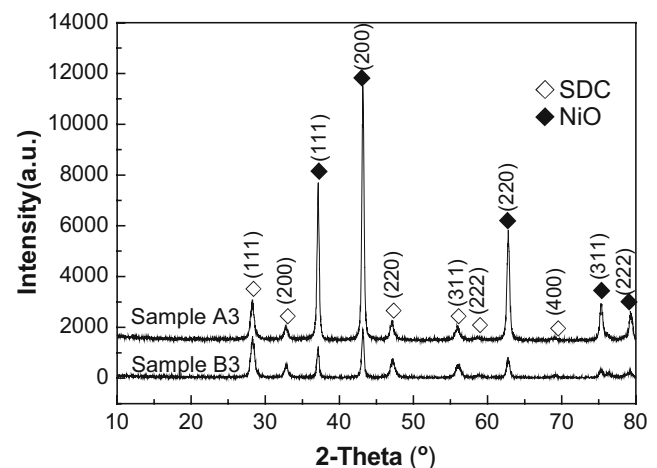
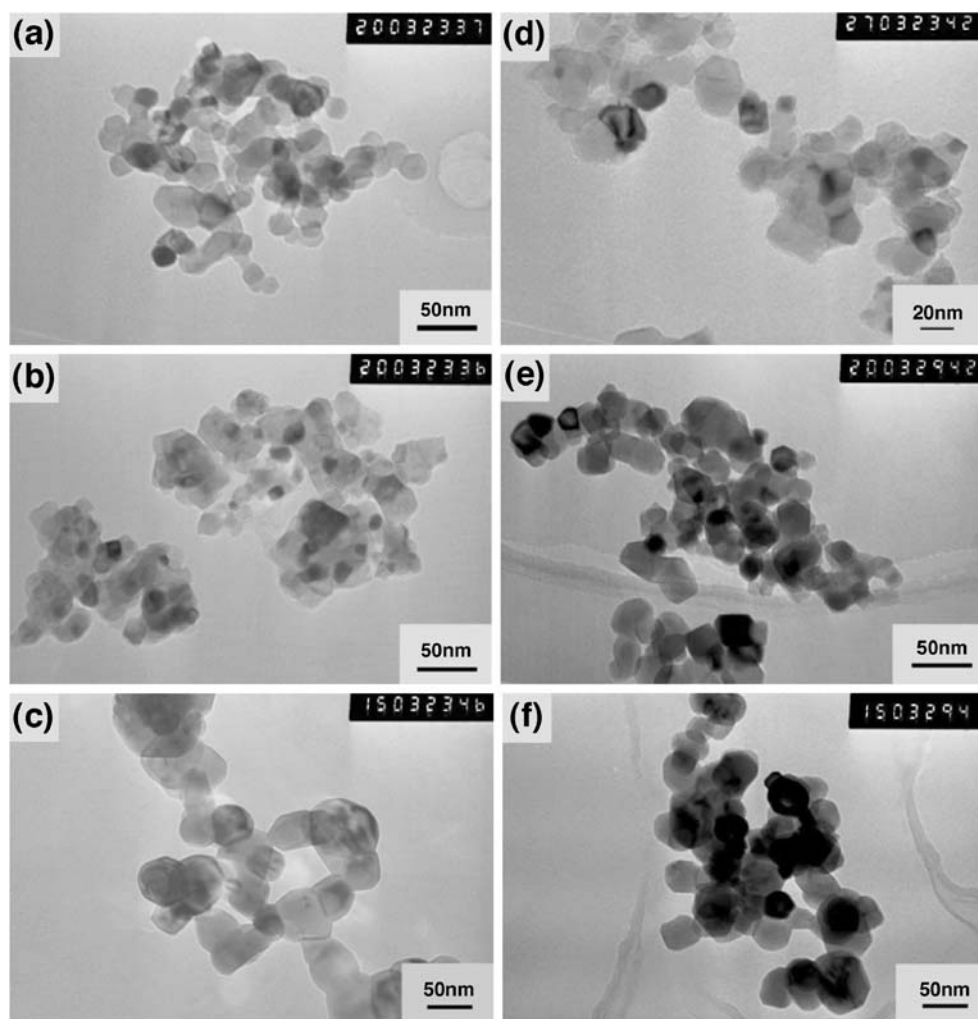
**Fig. 1** XRD patterns of NiO-SDC composite powders from two series

Fig. 2 TEM images of NiO-SDC composite powders from two series: (a) Sample A1; (b) Sample A2; (c) Sample A3; (d) Sample B1; (e) Sample B2; (f) Sample B3



4 Discussions

In colloidal spray pyrolysis, the chemical composition of sol particles in the spray colloidal solutions can affect the characteristics of the resulting powders including phase distributions. During the spray pyrolysis, salts in spray solutions precipitate on the surface of the sol particles [6]. As a result, the sol particles in calcined powders are covered by other particles derived from decomposition of the salts, and almost have no chance to grow up. They have a poor crystallinity. Contrarily, the particles formed by precipitation from spray colloidal solution have opportuni-

ties to grow and develop because these particles are easy to enrich on the surface of sol particles. Considering intrinsic growth ability, SDC are difficult to grow up [10]. Hence, the above mentioned can explain the following facts: the

Table 2 The average primary particle size of NiO-SDC composite powders from two series in Fig. 2.

	1	2	3
	(nm)		
Series A	25	30	56
Series B	24	29.5	44

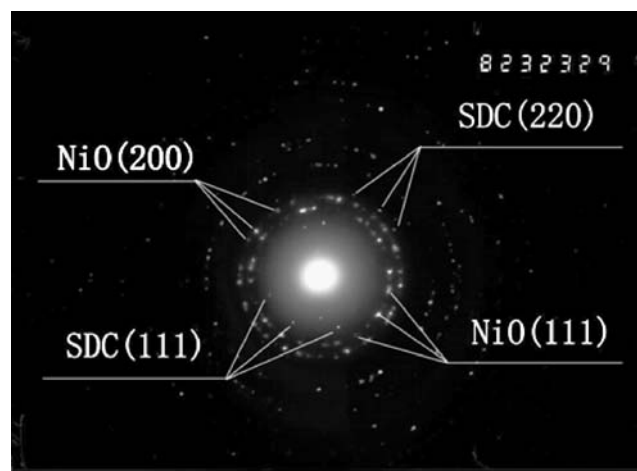


Fig. 3 The SAED pattern of NiO-SDC composite powders as shown in Fig. 2(f)

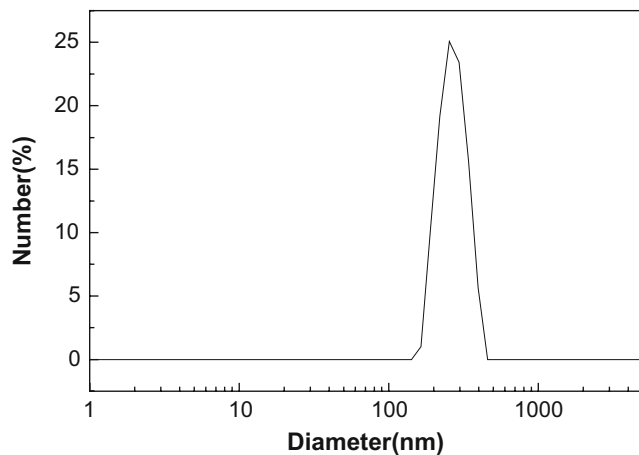


Fig. 4 The particle size distribution of NiO-SDC composite powders (Sample B3)

composite powders from series A have a high crystallinity of NiO (Fig. 1), those from series B have equivalent crystallinity for NiO and SDC (Fig. 1), and the primary particle sizes in the powders from series B are smaller than them from series A (Fig. 2 and Table 2). It can be concluded that the powders from series B are considered to be suitable to utilize in preparing the anodes of SOFCs.

Agglomerated particles in the powders from series B shows to have two phases of NiO and SDC (Fig. 3), this indicates that NiO and SDC primary particles are distributed very homogeneously, even in a 15×15 nm area as shown in Fig. 2(f). The narrow particle size distribution (Fig. 4) means that the powders have a weak aggregation.

5 Conclusions

Nanocrystalline NiO-SDC composite powders could be prepared by the present colloidal spray pyrolysis. The composite powders from spray colloidal solutions with Ni hydroxy carbonate sols were better than those with Ce-Sm hydroxy carbonate sols in crystallinity and primary particle size. The powders had a very narrow particle size distribution centered at 250 nm. The electron diffraction pattern showed that NiO and SDC primary particles are mixed very homogeneously in 250 nm aggregated particles. The powders are believed to be suitable to utilize in preparing the high performance anodes of SOFCs.

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