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Effect of powder preparation on (CeO₂)_{0.8}(Sm₂O₃)_{0.1} thin film properties by screen-printing

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Abstract

Chemical co-precipitation process and glycine-nitrate process (GNP) were used to synthesize $(CeO_2)_{0.8}(Sm_2O_3)_{0.1}(SDC)$ powders for the preparation of thin dense film by screen-printing. XRD, transmission electron microscope (TEM), scanning electron microscope (SEM) and the AC impedance spectroscopy were used to investigate the phase identification, morphology and electrical properties of SDC powders, respectively. It was found that the powders prepared by both processes possessed similar sinterability and conductivity. To both synthesized powders, the SDC pellets sintered at 1350 °C can reach 96% in relative density and 0.08 S cm⁻¹ in conductivity at 800 °C in air. Thin electrolyte films about 30 μ m have been successfully achieved by screen-printing with both powders. While the thin electrolyte film by GNP powders possessed better sinterability and higher conductivity, which was attributed to its high pack density during the green film preparation.

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1. Introduction

Solid oxide fuel cells (SOFCs) are promising and environmental friendly energy conversion systems with highenergy efficiency. However, the high operating temperature (up to 1000 °C) of traditional SOFCs with yttria stabilized zirconia (YSZ) as electrolyte can lead to complex materials problems. Doped ceria has attracted much attention in recent years, especially as a possible substitute of solid electrolyte to YSZ in SOFC application [1]. Its superior oxygen ion conductivity and lower interfacial losses with cathode and anode would allow to bring down the SOFC operating temperature from 1000 to 600-800 °C, which offers greater flexibility in the design of electrodes and in the choice of interconnector materials [2,3]. To intensively lower the working temperature of SOFC, thin electrolyte film is also necessary to reduce the ohmic resistance of the cell.

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Various techniques, such as tape casting and electrochemical vapor deposition, have been used to fabricate dense thin electrolyte films [3]. Compared with these filmpreparation techniques, the screen-printing technique could be a potential candidate for producing electrolytes in an inexpensive way.

It was reported that the morphology of powders had a great effect on the quality of the films prepared by screenprinting [4]. In our paper, two soft-chemical routes as coprecipitation and glycine-nitrate process (GNP) were used to synthesize the $(CeO_2)_{0.8}(Sm_2O_3)_{0.1}(SDC)$ powders. The properties of SDC powders were investigated and the effect of powder synthesis on the quality of thin electrolyte film prepared by screen-printing was also reported.

2. Experimental

2.1. Powders syntheses

Nano-ceramic powders of $(CeO_2)_{0.8}(Sm_2O_3)_{0.1}(SDC)$ were prepared by the oxalate co-precipitation route with the precursors of $Ce(NO_3)_3 \cdot 6H_2O$ and Sm_2O_3 . The stoichio-

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Fig. 1. XRD patterns of the SDC powders prepared by co-precipitation and GNP: (a) standard CeO₂; (b) SDC1; and (c) SDC2.

metric starting materials were dissolved in the dilute nitrate acid, and then dripped to the oxalic acid solution, which was adjusted to neutral pH (6.6–6.9) by dilute ammonia solution. After fully washed by water and ethanol, the precipitate was calcined at 750 °C for 2 hr with the heating rate of 3 °C/min to form the cubic fluorite structure. SDC powders prepared by co-precipitation were remarked as SDC1.

Stoichiometric amount of $Ce(NO_3)_3 \cdot 6H_2O$ and Sm_2O_3 was dissolved in dilute nitrate acid. Glycine (NH_2-CH_2-COOH) was then added to the solution, and the molar ratio of glycine to metal ions was set to 1.7 according to the calculation [5]. The stirred solution was heated on a hot plate, converted to a viscous gel due to evaporation, and ignited to flame, resulting in fine SDC "ash" of pale-yellow in color. The "ash" was calcined at the temperature from 750 °C for 2 h to remove any carbon residues remaining in the ash and to form a well crystalline structure. The SDC powders synthesized by GNP were noted as SDC2.

Calcined SDC1 and SDC2 powders were cold pressed at 220 MPa into cylindrical pellets (13 mm in diameter and 1 mm in thickness). The green SDC pellets were then sintered at 1350 $^{\circ}$ C for 5 h with a heating rate of 3 $^{\circ}$ C/min.

2.2. Thin electrolyte film preparation

Screen-printing technique was used to prepare thin electrolyte on the porous NiO/SDC substrate with the SDC1 and SDC2 powders. The slurry consisting of SDC powders, ethocel, and abietyl alcohol was screen-printed onto the substrates to form a thin electrolyte film. The bilayer was then dried, and sintered at 1350 °C for 5 h at a heating rate of 1 °C/min, and adwell at 350 °C for 2 h to remove the organics.

2.3. Characteristics

X-ray diffraction (D/Maz- γ_A X diffractometer with Cu K α radiation) was used to confirm the crystalline structure of the calcined powders. The particle size and morphology of the powders were examined with a transmission electron microscope (TEM, Hitch 800, Japan). A scanning electron microscope (SEM, Hitch 650) was used to detect the microstructure of the sintered pellets and the films. The relative densities of the sintered pellets were determined by standard Archimedes' method. Conductivity of the specimens was determined from the impedance measurement



Fig. 2. TEM photographs of Sm_{0.2}Ce_{0.8}O_{1.90} powders calcined at 750 °C: (a) SDC1 and (b) SDC2.



Fig. 3. SEM photographs of SDC pellets sintered at 1350 °C for 5 h: (a) SDC1 and (b) SDC2.

(Genrad 1689) from 450 to 800 $^{\circ}$ C in air at a controlled heating rate. Before measurements, platinum electrodes were prepared by painting platinum paste onto either side of the pellets, and firing at 900 $^{\circ}$ C for 1 h.

Platinum paste was spread on the surface of the sintered thin SDC film and fired at 900 $^{\circ}$ C for 1 h. Conductivity of the films was determined by the impedance measurement from 450 to 800 $^{\circ}$ C in hydrogen at a heating rate of 5 $^{\circ}$ C/min.

3. Results and discussion

3.1. Powders characteristic

As shown in Fig. 1, SDC1 and SDC2 powders calcined at 750 °C possessed the cubic fluorite structure with broad



Fig. 4. Temperature dependence of the electrical conductivity of SDC pellets prepared by different methods and sintered at 1350 $^\circ C$ for 5 h.

peaks. After sintered at 1350 °C, these specimens were well crystallized, and the sharp X-ray peaks give their cubic lattice parameter *a* of SDC 5.412 Å. For the assumed solid solution, the theoretical density was calculated to be 7.222 g/cm³ according to Eq. (1):

$$D_{\rm th} = 4 \times [(1 - x)M_{\rm Ce} + xM_{\rm Sm} + (2 - 0.5x)M_{\rm O}] / (N_{\rm A} \times a^3), \tag{1}$$

where x is the molar percent of Sm, N_A is Avogadro's constant, M_i refers to atomic weights of Ce, Sm and O.

Fig. 2 presents the TEM photograph of SDC powders prepared by both process and calcined at 750 $^{\circ}$ C for 2 h. As shown in Fig. 2(a), the calcined SDC1 powders present fantastic pillar forms. To the SDC2 powders, a foam-like morphology was observed with a weak force among little grains, as shown in Fig. 2(b). The loose structure and the weak bonds among the powders seemed to result from the great amount of gases released by the redox reaction [5].

3.2. Properties of sintered pellets

Though the two preparation processes made a big difference in the morphology of SDC1 and SDC2 powders, but it seems that they had little effect on the sinterability and conductivity of SDC pellets. The relativity of SDC1 and SDC2 pellets sintered at 1350 °C for 5 h were measured by

Table 1					
The conductivity of S	DC pellets	sintered at	1350	°C for	5 h

Conductivity (S cm ⁻¹)	500 °C	600 °C	700 °C	800 °C	Activation energy (kJ/mol)
SDC1	0.00507	0.01959	0.04638	0.08981	75.17
SDC2	0.00408	0.01576	0.04149	0.08180	78.65

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Fig. 5. SEM photographs of the thin film fracture prepared by screen-printing with various SDC powders: (a) SDC1 and (b) SDC2.



Fig. 6. Magnified photographs of the thin film prepared by screen-printing with various SDC powders: (a) SDC1 and (b) SDC2.



Fig. 7. SEM photographs of the surface of green SDC film prepared by screen-printing with various SDC powders: (a) SDC1 and (b) SDC2.

Table 2 The resistance of thin SDC film prepared on the porous Ni/SDC substrate with various powders

Conductivity (S cm ⁻¹)	500 °C	600 °C	700 °C	800 °C
SDC1	0.00207	0.00709	0.02331	0.04681
SDC2	0.00322	0.01067	0.03549	0.06081

the standard Archimedes' method to be 96.6% and 96.4%, respectively. The SEM photographs of pellets' fracture also revealed that the two pellets were very dense, as shown in Fig. 3.

Fig. 4 presents the conductivity of sintered SDC1 and SDC2 pellets measured by AC impedance spectroscopy from 450 to 800 °C in air. The conductivity of the two pellets was quite close which was in accordance with their density. Table 1 gives the conductivity values of SDC1 and SDC2 pellets from 500 to 800 °C, in which SDC1's conductivity was a little higher than that of SDC2.

3.3. Thin electrolyte film

Gas-tight thin films about 30 µm in thickness were prepared by screen-printing onto the NiO/SDC substrates, following the sintering of 1350 °C for 5 h. As shown in Fig. 5, the thin films prepared by both SDC1 and SDC2 were quite dense and uniform. However, from the magnified fracture SEM photographs (Fig. 6), it could be clearly seen that thin film prepared by SDC2 powders was less porous than that by SDC1, though the cold-pressed pellets made by them had quite similar sinterability. SEM was used to investigate the green electrolyte films. From the surface of the green thin film prepared by SDC1 and SDC2 (shown in Fig. 7), it was found that the foam-like morphology of SDC2 powders had been totally broken into small particles after milling in the slurry which helped to enhance the pack density. While in Fig. 7(a), the SDC1 remained the pillar structure, which provides much more pores and restrains the densification during sintering. It was deduced that the high pressure used in cold-pressing of the SDC pellets helped to break both the foam-like morphology of SDC2 and the pillar structure of SDC1, so they have almost the same sinterability and conductivity.

The conductivity of the films was measured by AC impedance spectra. As measured in H_2 , NiO was totally

reduced to be Ni, and it was assumed that all the resistance of the specimens came from the ohmic resistance of SDC thin film. Table 2 presents the conductivity of the specimen. It was found that the conductivity of the thin film prepared by SDC2 was much higher than that by SDC1, which was consistent with the film density.

4. Conclusions

 $(CeO_2)_{0.8}(Sm_2O_3)_{0.1}$ powders were prepared by the oxalate co-precipitation route and nitrate-glycine process. Very different morphology was found for the two kinds of powders, as fantastic pillar for SDC1 and foam-like structure for SDC2. Though the pellets prepared by SDC1 and SDC2 had almost the same sinterability and conductivity, the thin electrolyte films of SDC2 prepared by screenprinting were quite denser than that of SDC1. From the SEM photographs, it could be found that the foam-like morphology of SDC2 had been totally broken into small particles after milling in the slurry. It was deduced that the small particles helped to enhance the pack density and sinterability of the film. The conductivity of SDC2 film was also higher than that of SDC1 film, which was in accordance with their relative density.

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