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Sintering and electrical properties of $(CeO_2)_{0.8}(Sm_2O_3)_{0.1}$ powders prepared by glycine–nitrate process

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Abstract

$(CeO_2)_{0.8}(Sm_2O_3)_{0.2}$ (SDC) powders were prepared using the glycine–nitrate process (GNP) with different glycine/metal ratios. The phase identification, morphology and electrical properties of SDC powders were investigated by XRD, TEM and the AC impedance spectroscopy, respectively. It was found that the ratio of glycine/metal had a great effect on both the morphology and the sinterability of the powders as well as the conductivity of the sintered pellets. When the ratio is around the stoichiometric value (about 1.6), the loose powders possessed a foam-like structure. The bulk density of SDC pellets sintered at 1500 °C could reach 95% only when the ratio of glycine to metal was in the range of 1.3–2.0. The conductivity increased with the ratio of glycine to metal till at the ratio of 1.7, and then decreased. The maximum conductivity of the sintered specimens was 0.082 Scm^{-1} at 800 °C.

Keywords: Solid oxide fuel cell; Electrolyte; $Sm_{0.2}Ce_{0.8}O_{1.9}$; Glycine–nitrate process; Conductivity

1. Introduction

Doped ceria, as a possible substitute electrolyte for solid oxide fuel cells, has received much interest now. Compared with traditional stabilized zirconia electrolyte, doped ceria electrolyte presents the advantages of superior conductivity and better compatibility with the electrodes, which allows for a reduction of operating temperatures from 1000 to 600–800 °C or even lower. Thus, some serious problems caused by the high operating temperature, such as electrode sintering, interfacial diffusion between electrolyte and electrodes and mechanical stress due to thermal mismatch between neighboring components, can be alleviated.

Some wet chemical processes, such as hydrothermal synthesis and homogeneous precipitation [1,2], have been adopted to prepare fine doped-ceria powders with good sinterability. Recently, the glycine–nitrate process (GNP) has been introduced as one of a general class of combustion methods for the preparation of ceramic powders [3]. GNP is a relatively inexpensive preparation technique to produce fine, homogeneous powders and has been used to prepare simple oxides as well as multi-component oxides successfully [4–6].

It was found that the ratio of glycine to metal had a great effect on the properties of the prepared powders, but no systemic result had been reported. In this paper, we studied the morphology and sintering behavior of

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$Sm_{0.2}Ce_{0.8}O_{1.9}$ powders with the ratio of glycine to metal.

2. Experiment

To prepare $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) powders by GNP, stoichiometric amount of $Ce(NO_3)_3{\cdot}6H_2O$ and Sm_2O_3 were dissolved in dilute nitrate acid. Glycine (NH_2-CH_2-COOH) was then added to the solution. The molar ratio of glycine to metal was set from 0.7 to 3.4. The solution was heated on a hot plate under stirring, 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 to 1000 °C for 2 h to remove any carbon residues remaining in the ash and to form a well-crystalline structure. The calcined powders were uniaxially pressed under 220 MPa to form pellets of 13 mm in diameter and 1 mm in thickness, and then sintered at 1500 °C for 5 h with a heating rate of 3 °C/min.

The phase identification of SDC powders was made with the powder X-ray diffraction using CuK_α radiation (D/Max-γA, Japan). The morphology of the powders was observed using a transmission electron microscope (TEM, Hitch 800). The relative densities of the sintered pellets were measured by the standard Archimedes' method. A scanning electron microscope (SEM, Hitch 650) was used to detect the microstructure of the sintered pellets. Conductivity of the specimens was determined by the impedance measurement (GenRad 1689 Precision RLC Digibridge) from 450 to 800 °C in air. The frequency range covers from 12 Hz to 100 kHz. Before measurements, platinum electrodes were prepared by painting platinum paste onto both sides of the pellets, and then fired at 900 °C for 1 h.

3. Results and discussion

GNP is a self-sustaining combustion synthesis technique, containing metal nitrates as oxidizers and glycine as a fuel. Therefore, the ratio of glycine to metal is of great importance to complete the oxidation–reduction reaction completely [4]. In this process, glycine serves dual roles. In the precursor solution, the glycine complexes the metal cations, thereby preventing selective precipitation. While igniting, the glycine is oxidized by the nitrate anions, serving as the fuel for the combustion reaction. The combustion process is an exothermic redox reaction, in which the flame temperature can reach 1100–1400 °C affected by the ratio of glycine to metal and reach maximum at the proper ratio [5,6].

Assuming that the sole gaseous products of combustion were H_2O, CO_2 and N_2, with all glycine fuels stoichiometrically oxidized by nitrates, the reactions can be expressed as follows, and the stoichiometric ratio is calculated as below:

$$Ce(NO_3)_3 + NH_2 - CH_2 - COOH \rightarrow CeO_2 + H_2O + N_2 + CO_2 \quad (1)$$

$$(\text{glycine}/Ce^{3+} = 14/9 \approx 1.56)$$

$$Sm(NO_3)_3 + NH_2 - CH_2 - COOH \rightarrow Sm_2O_3 + H_2O + N_2 + CO_2 \quad (2)$$

$$(\text{glycine}/Sm^{3+} = 15/9 \approx 1.67)$$

The required ratio of glycine/metal is calculated to be 1.58 according to Eqs. (1) and (2) and the ratio of Ce^{3+}/Sm^{3+} in the precursor solution.

As shown in Fig. 1, all the calcined powders exhibited a well-cubic fluorite structure, which was not affected by the ratio of glycine to metal. The theoretical density of the SDC specimens was determined to be 7.22 g cm^{-3} with the lattice parameter calculated from the XRD measurements.

The ratio of glycine to metal affected the products' morphology. Fig. 2 showed the TEM photographs of the calcined SDC particles prepared by GNP. When the glycine-to-metal ratio was around the theoretical calculation value (about 1.6), highly loose particles with a foam-like morphology and a weak force among them were observed, as shown in Fig. 2(b). While dense polygonal particles were obtained for the ratio either too high (≥ 3.4) or too low (≤ 0.7), shown in Fig. 2(a) and (c). The loose structure and the weak bonds among the powders shown in Fig. 2(b) seemed to result from the great amount of gases released by the redox reaction. Meanwhile, at low ratio, the glycine was possibly too scarce for the reduction of

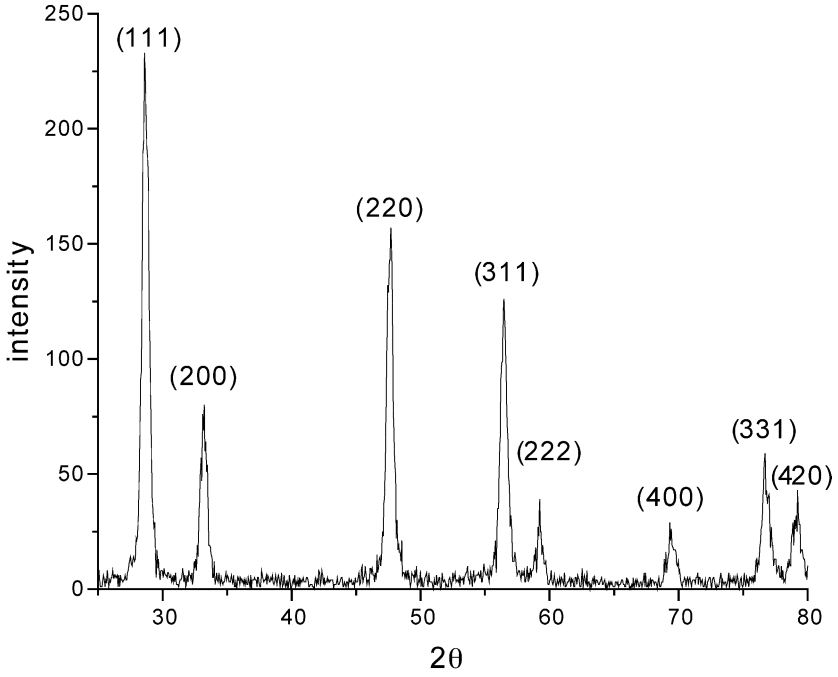

Fig. 1. XRD patterns of calcined SDC powders with different glycine-to-metal ratio. (a) The ratio of 0.7, (b) the ratio of 1.7, and (c) the ratio of 3.4.

NO_3^-, so the viscous precursor released much less gases and combusted slowly, thus it cannot form highly porous particles but relatively dense particles with size of 10–20 nm, as shown in Fig. 2(a). In contrast, at high ratio, the NO_3^- could not be reduced completely (NO_x yielding), and the oxidation of the

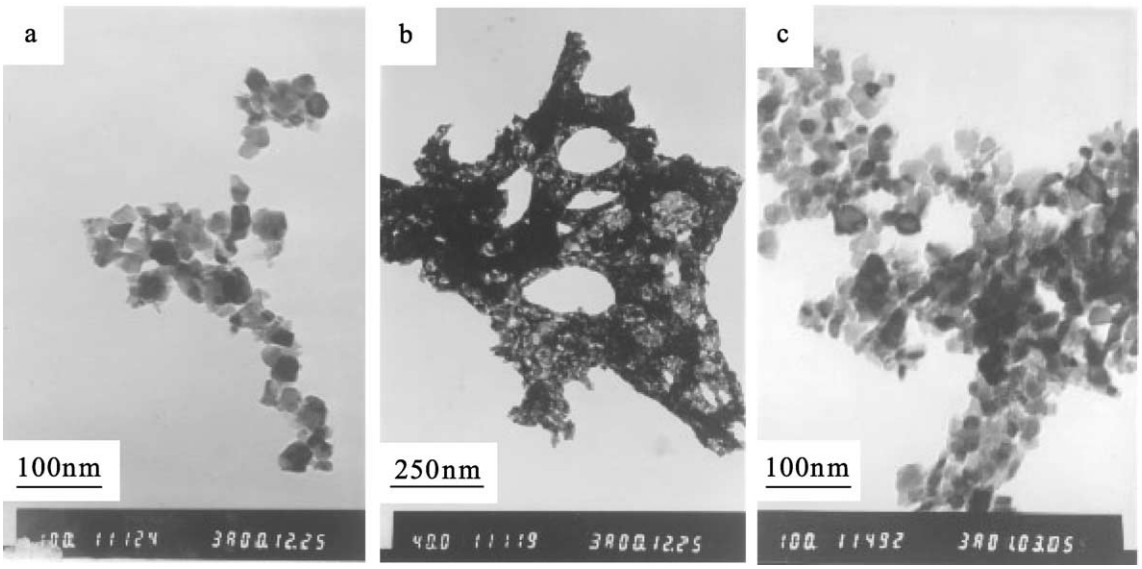

Fig. 2. TEM photographs of SDC powders heated at 750 °C. The powders were prepared with glycine-to-metal ratio of (a) 0.7, (b) 1.7, and (c) 3.4.

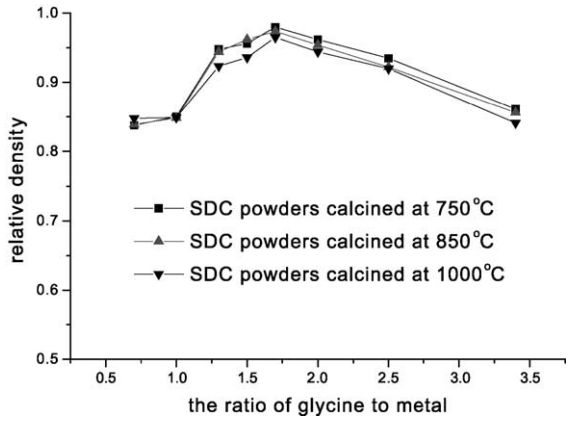

Fig. 3. Relative densities of SDC sintered at 1500 °C for 5 h as a function of calcination temperature and the ratio of glycine to metal.

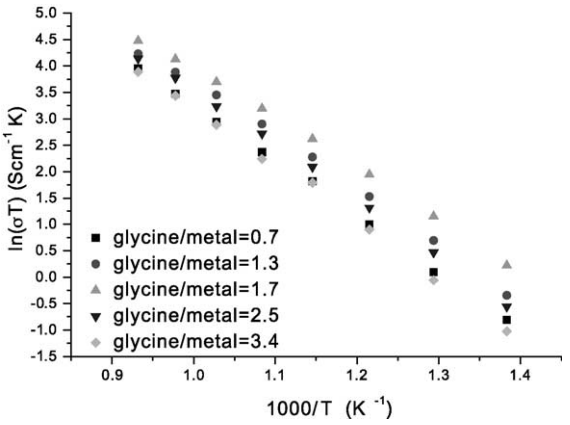

Fig. 5. Temperature dependence of the electrical conductivity of SDC pellets prepared by different ratios of glycine to metal and sintered at 1500 °C for 5 h.

glycine needed the atmospheric air, which also degraded the release of the heat and gas.

The powders' sinterability was also affected by the ratio of glycine to metal. The relative densities of SDC pellets sintered at 1500 °C for 5 h were plotted in Fig. 3 as a function of glycine-to-metal ratio. Relative densities higher than 95% were achieved at the ratio from 1.3 to 2.0. While the ratio is too low (0.7 and 1.0) or too high (3.4), the relative density is only about 85%. It is also noted that the temperature of calcination had little effect on the sintered density.

Fig. 4 gives the SEM images of the sintered SDC specimens prepared with different glycine/metal ratios. As shown in Fig. 4(b), the SDC pellets with the ratio of 1.3–2.0 presented high density, just with little closed pores. While the ratio is 0.7 or 3.4, there were many pores in the body of those pellets, shown

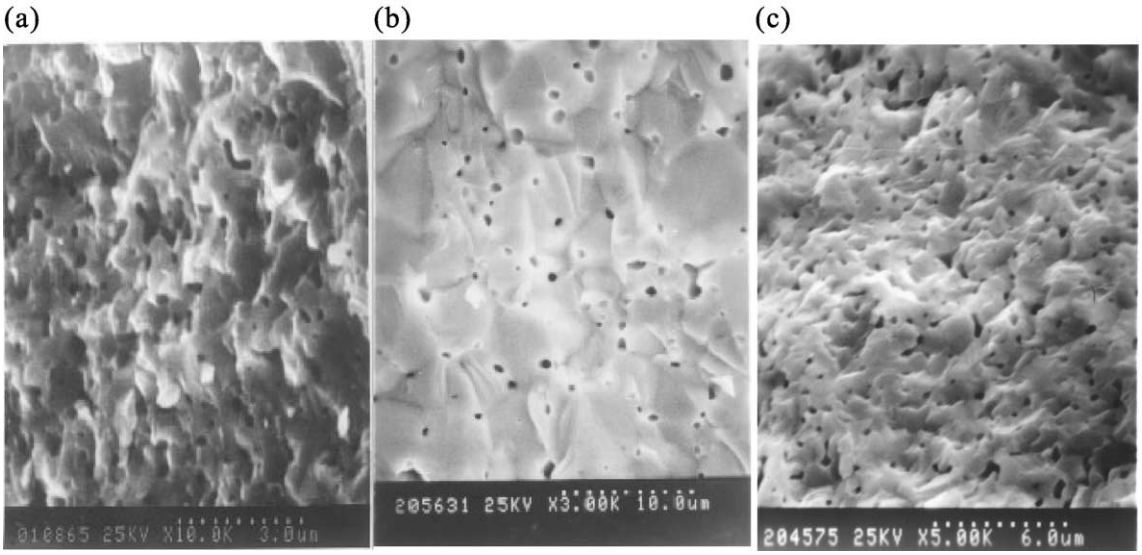

Fig. 4. SEM images of $Sm_{0.2}Ce_{0.8}O_{1.9}$ pellets' fracture at different ratios sintered at 1500 °C for 5 h. (a) The glycine/metal ratio of 0.7, (b) the glycine/metal ratio of 1.7, (c) the glycine/metal ratio of 3.4.

Table 1
The conductivity of SDC as function of the glycine/metal ratio

	Conductivity (Scm^{-1})			Activation energy (kJ/mol)
	600 °C	700 °C	800 °C	
SDC07	0.007	0.019	0.048	87.9
SDC13	0.011	0.032	0.064	84.8
SDC17	0.016	0.041	0.082	78.7
SDC25	0.009	0.026	0.058	86.9
SDC25	0.006	0.018	0.045	90.7

The number after SDC is the ratio of glycine to metal times 10.

in Fig. 4(a) and (c). Those SEM images were quite in accordance with their relative densities.

The conductivity of sintered pellets was also different with different ratios of glycine to metal. Fig. 5 presented the Arrhenius plots for sintered SDC specimen prepared by different ratios of glycine to metal. Table 1 gives the conductivity values of $Sm_{0.2}Ce_{0.8}O_{1.9}$ pellets at 600, 700 and 800 °C. It was obvious that the conductivity first increased with the ratio of glycine to metal and then decreased, reaching maximum at the ratio of 1.7, quite in correspondence with the stoichiometric value. Meanwhile, the activation energy of the conductivity reaches the minimum value of 78.7 kJ/mol at the ratio of 1.7. The relative density of the specimens seems to be responsible for the difference between the conductivity.

4. Conclusion

Ultra-fine $Sm_{0.2}Ce_{0.8}O_{1.9}$ powders were successfully synthesized by the glycine–nitrate process. The relative densities of SDC pellets prepared with such powders and sintered at 1500 °C cannot exceed 95% unless the ratio of glycine to metal is 1.3–2.0, which is around the stoichiometric data (about 1.6). The conductivity of such pellets first increases with the ratio of glycine to metal, reaching the maximum value of 0.082 Scm^{-1} at the ratio of 1.7, and then decreases, which is quite consistent with the specimens' porosity. Therefore, the proper ratio of glycine to metal is essential in the glycine nitrate process.

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