Nanocrystals-Based Macroporous Materials Synthesized by Freeze-drying

Combustion

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Abstract

We present a novel freeze-drying combustion method for synthesis of macroporous powders with nano-network, using $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$, SDC as an example. The metal nitrate salt solution mixed with glycine is frozen to form homogeneous nitrate/glycine mixture and then freeze-dried through sublimation of ice crystals. Upon combustion of the freeze-dried mixture, SDC powders with macroporous microstructure consisting of 10-20 nm nanocrystals, high surface area and excellent sinterability are achieved. High resolution transmission electron microscopy (HRTEM) analysis indicates that nanodomains due to aggregation/segregation of dopants in the SDC powders obtained from freeze-drying combustion are much smaller than those in the SDC powders synthesized by the conventional nitrate solution combustion approach, demonstrating better elemental homogeneity and improved conductivity. Using low cost precursors and simple processing conditions, freeze-drying combustion can be a versatile method to synthesize nanocrystalline powders with excellent composition homogeneity for broad applications.

Keywords:

Solid oxide fuel cell; $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$; Freeze-drying combustion; Nano-network

1. Introduction

Nanoscale materials have been widely developed as catalysts for their advantageous catalytic properties[1-10]. Various wet chemistry approaches have been developed to synthesize nanoparticles, such as hydrothermal[11], co-precipitation[12] and solution combustion[13]. The powders prepared by the aforementioned methods are usually composed of very small nanocrystals, which are beneficial for dense film preparation at lower sintering temperatures[14]. The extremely fine and loose powders obtained from solution combustion typically possess high surface area, favorable for the electrochemical reactions when these powders are used as catalysts and electrodes in energy conversion and storage devices[15-20]. However, some of the solution combustion methods require stringent process controls and are challenging for broad commercialization. Glycine-nitrate process (GNP) is one of the most commonly used solution combustion approach in preparation of nanoscale materials/electrodes for solid oxide fuel cell (SOFC) applications[21]. The metal nitrates dissolved in water are mixed homogeneously at the atomic scale and chelated by glycine, yielding desired stoichiometry. However, during the removal/evaporation of water by heating the solution, the stability of the gel becomes an issue and some metal salts precipitate selectively, producing agglomerated oxide powder mixture with some minor composition inhomogeneity [22]. The composition inhomogeneity can be eliminated by high temperature calcination, however, which will result in a significant reduction in surface area and coarsening of the powders. Further, aggregation/segregation of dopants during the drying of the metal nitrate/glycine gel can lead to formation of nanodomains and decrease the mobility of oxygen vacancy, and consequently decrease ionic conductivity[23]. It has been expected that powders with superior performance would be created when the size of domains can be controlled in the

subnano level[24]. In addition, the glycine/nitrate approach involves water-based solution and it is very challenging to scale-up nanopowder synthesis. Therefore, a liquid-free combustion method enabling large scale high quality nanoparticle synthesis is of great significance.

Freezing has been developed as an effective path to build complex porous composite[25, 26]. In sea ice, the various impurities (salt, biological organisms, etc.) originally present in sea water are expelled from the forming ice and entrapped within tiny channels between the ice crystals[27]. The impurities are all concentrated in the interstices between ice platelets. Inspired by this natural principle, we developed a new solid combustion, freeze-drying combustion for synthesis of nanoparticles. Nitrate solution is frozen and ice is applied as the template or cage to fix glycine-metal mixture, preventing aggregation/agglomeration and enhancing the complex stability. After sublimation of ice by freeze drying under vacuum, the metal/glycine mixtures are distributed in a macroporous scaffold whose microstructure is a negative replica of the ice. Afterwards, glycine acts as fuel during combustion reaction, being oxidized by the nitrate ions. Both the ice and glycine in this freeze-drying combustion process helps the formation of extremely fine oxide powders by impeding the internal complex/particles contact. Meanwhile, the powders are expected to show homogeneous element distribution since the atomic-level mixture was frozen from liquid into solid in several seconds.

Ceria based materials have been considered as the most promising electrolyte for low temperature SOFCs due to the higher oxygen ion conductivity at 400-600 °C compared to yttria-stabilized zirconia (YSZ)[28, 29]. In this report, we have synthesized $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) nano-particles through freeze-drying combustion (FC). The powder made by FC is denoted as SDC-FC. The novel method shown herein offers a simple way to produce porous nano powders in a large scale. The as-prepared powders are extremely loose, making it easier to obtain thin dense films using a low cost co-pressing and co-sintering method. Furthermore, the high

resolution transmission electron microscope (HRTEM) analysis indicates that the nanodomains in SDC-FC powders are much smaller than those in SDC powders synthesized by GNP (denoted as SDC-GNP), indicating a good dopant distribution.

2. Experimental and Characterization

$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were purchased from Alfa Aesar (USA) and dissolved in deionized water in a desired stoichiometric ratio. The glycine was added into the solution with half mole of nitrate ions. The mixture solution was stirred for 10 hours and then poured and frozen on a Mylar film on a freezing bed ($-70\text{ }^\circ\text{C}$) for 1 h. The solid ice/nitrate was then moved into a vacuum chamber at $-30\text{ }^\circ\text{C}$ for 12 h and then at $+30\text{ }^\circ\text{C}$ for another 12 h under vacuum of 100 mtor. The macroporous glycine/nitrate mixture was then quickly moved to a microwave oven and treated for self-combustion. For comparison, the SDC powder was also synthesized by traditional glycine nitrate process (GNP) with assistance of microwave oven. The porous ashes were then heat-treated at $600\text{ }^\circ\text{C}$ for 2 h. The obtained SDC powders were pressed into pellets and sintered at $1300\text{ }^\circ\text{C}$, $1350\text{ }^\circ\text{C}$ and $1400\text{ }^\circ\text{C}$ for 5 h, respectively. The density of the sintered samples was determined by the Archimedes method. The sintering behaviors of SDC-FC and SDC-GNP were characterized by a NETZSCH DIL 402C pushrod dilatometer at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. NiO-GDC substrate was obtained by uniaxially pressing of a ball-milled mixture of NiO (Sigma–Aldrich, USA) and GDC powder (Fuel Cell Materials, USA) with 20 wt% graphite powder. A thin layer of loose SDC powder was distributed uniformly on the anode substrate and then co-pressed with anode substrate[30]. The bi-layer was subsequently sintered at 1200

°C for 5 h, resulting in a dense SDC electrolyte film on NiO-GDC substrate. La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF)-GDC (mass ratio of 1:1) cathode with an active area of 0.33 cm² was prepared on the GDC electrolyte surface by brush-painting and then fired at 1050 °C for 2 h. Silver paste was brushed on cathode surface and sintered at 800 °C.

The crystalline structure of SDC powders (annealed at 600 °C for 2 h) was studied by X-ray diffraction (XRD) analysis over the 2 θ range of 20-80 degree with a scanning rate of 2 degree min⁻¹ on a D/MAX-3C X-ray diffractometer with graphite-monochromatized CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The microstructure of the fuel cells was characterized using a scanning electron microscope (SEM, Zeiss Ultra plus FESEM). High resolution transmission electron microscopy (HRTEM) image of SDC powders was acquired using a JEOL 2100F TEM equipped with a Schottky field-emission gun (FEG) with Cs=1.0 mm operated at 200 kV. The specific surface areas of the SDC powders obtained from the two different approaches were determined using a Quantochrome NOVA 2000 high-speed surface area analyzer. For conductivity measurement, both sides of the sintered SDC pellets were coated with Pt paste and heat-treated at 1000 °C for 30 min before testing. Electrical conductivity was measured using A.C. impedance method with A.C. amplitude of 10 mV in the frequency range from 0.1 Hz to 1 MHz using a Zahner IM6 Electrochemical Workstation (ZAHNER-Elektrok GmbH & Co., Kronach, Germany). The conductivity is obtained using the following equation:

$$\sigma = \frac{L}{RA} \quad (1),$$

where σ is the conductivity, R is the resistance, L is the sample thickness, and A is the sample area. The current density-voltage curves as well as impedance spectra of the fuel cells were measured with a four probe method using a multi-channel Versa STAT (Princeton Applied Research) at an operating temperature range of 500-600 °C. Humidified (3 vol% H₂O) hydrogen was used as fuel while ambient air was used as oxidant. Hydrogen flow rate was controlled at 40 sccm by a mass flow controller (APEX, Alicat Scientific). The electrochemical impedance spectra of cells were measured under open circuit voltage over a frequency range of 1 MHz to 0.1 Hz. The interfacial polarization resistance (R_p) was determined from the difference between the low and high frequency intercepts of the impedance spectra with the real axis in the Nyquist plot.

3. Result and Discussion

Figure 1 (a) shows the XRD patterns for the SDC-FC powder fired at 600 °C, indicating excellent crystallinity. The sample exhibits XRD peaks that correspond to a cubic fluorite structure of Sm_{0.2}Ce_{0.8}O_{1.9}, as identified using the standard PDF Card (JCPDS 75-0158). The lattice parameter a calculated from the XRD spectra is 0.5432 nm. It is noticed that the a for SDC is larger than that for pure ceria (JCPDS 34-0394) which can be attributed to the lattice expansion caused by larger size of Sm²⁺ (0.1079 nm) than Ce⁴⁺ (0.0971 nm). The crystal size for SDC-FC calculated from X-ray line broadening of the (111) reflection by Scherrer's equation is 19.5 nm, smaller than that for the SDC-GNP (26.8 nm). Figure 1 (b) shows the SEM image, while Figure 1 (c, d) show the Bright Field, HRTEM images and the selected area electron diffraction (SAED) pattern for SDC-FC powder. The ring pattern was carefully measured and compared with JCPDS-PDF No. 75-0158 (SDC). The specific surface area (S_{BET}) for SDC-FC powder heat-treated at 600 °C is 34.9 m²g⁻¹, while the one for SDC-GNP powder is 25.1 m²g⁻¹. Particle size of the powder (D_{BET}) was 23.81 nm according to $D_{\text{BET}} = 6000 / \rho_{\text{th}} S_{\text{BET}}$, where ρ_{th} is the theoretical density. If defining $\psi = D_{\text{BET}} / D_{\text{XRD}}$ as

the factor to reflect the agglomeration extent of the primary crystalline[12], the ψ value of 1.0 indicates no agglomeration among crystallites. In this work, $\psi=1.22$ was achieved, which indicated softer agglomeration and better dispersion of the powders. Compared with the SEM and TEM images for SDC-GNP powder (Figure 2), it is shown that a much finer nanocrystals-based macroporous network can be efficiently generated by freeze-drying combustion.

Nanodomains with short-range ordered structure have been widely observed in the rare-earth doped ceria due to the aggregation/segregation of dopant cations (resulting from the inhomogeneous distribution) together with associated charge-compensating oxygen vacancies[31]. The formation of nanodomains can lead to lattice distortion or reorientation of fluorite structure[32], and decrease the ionic conductivity by reducing the mobility of oxygen vacancies in grain interior or boundary[23]. Therefore, it is of great significance that the size of the nano-domains could be controlled or decreased. It has been expected that superior quality electrolyte would be created when the size of domains is in the subnano level[24]. Figure 3 (a) shows the HRTEM image of SDC-FC powder. It can be found that the nanodomains (in red circles) with size ranging from 0.7-2 nm. By contrast, the nanodomains in SDC-GNP powder as shown in Figure 3 (b) have size ranging from 1.6-3.5 nm. Such a big difference could be attributed to the increased stability of the glycine-nitrate complex due to the protection from ice in the powder fabrication process. The liquid glycine-nitrate mixture can be frozen into solid ice-glycine-nitrate mixture in 1-2 seconds, thus avoiding the aggregation/precipitation of metal ions in conventional liquid combustion. It can be concluded that solid freeze-drying combustion can not only produce fine nanoparticles but also decrease the size of the nanodomains. Both of them could be beneficial to better sinterability and higher conductivity.

Figure 4 (a-c) shows the surface and cross-section (insets) SEM images for pellets made from SDC-FC powders sintered at different temperatures. Nearly theoretical density (98.9 %) was obtained when the pellets were sintered at 1400 °C, which can

only be achieved by sintering SDC pellets at 1500 °C for the SDC powder prepared by other methods [6, 33]. SDC-FC powder shows much better sinterability compared with SDC-GNP powder (Figure 5). The sinterability difference could be further confirmed by the dilatometric curves (Figure 4 (d)) for the two pellets prepared from SDC-FC and SDC-GNP. For SDC-FC pellets, the dimension seems to keep unchanged after 1343 °C, which is much lower than that (1452 °C) for pellets from SDC-GNP powder. The difference can be attributed to the difference of SDC particle size. Generally, the sintering rate increases with decreased particle size[34]. The effect of particle size on sintering can be explained by Herring's scaling law[35] at final stage of sintering,

$$\frac{1}{\rho} \frac{d\rho}{dt} \propto \frac{1}{G^m} \quad (2)$$

where ρ is the density, G is the grain size, and m is an exponent. Equations (2) indicates that the finer powder shows much faster sintering kinetics. The pellets from SDC-FC powder have a density of 98.9 %, higher than that for SDC-GNP (94.5 %) powder, confirmed by the cross-section SEM images (Figure 5 (b)).

Figure 6 shows the total conductivity of SDC pellets in air as the function of temperature. The conductivity values have been normalized by density. The conductivity of all the pellets increases with the temperature due to the thermal activated oxygen vacancy transference process. The pellets sintered at 1400 °C from SDC-FC show the conductivity of 0.018 Scm⁻¹ at 600 °C, higher than the one for the pellets from SDC-GNP powder (0.012 Scm⁻¹). All these values are comparable with those reported by others [6, 33, 36]. The activation energy for conduction measured for samples sintered at different temperatures was between 0.60 to 0.69 eV, which was lower than other works [12, 37]. The higher conductivity and lower activation energy can be attributed to the higher density or smaller nanodomains. Pellets from SDC-FC show a density of 98.9 %, while pellets from SDC-GNP show a density of 94.5 %. The smaller nanodomains indicate a better dopant distribution and a higher quality microstructure, thus mobility of oxygen vacancies will not be decreased.

Electrolyte materials with higher ionic conductivity have more potential to exhibit excellent electrochemical cell performance at low temperature. It is generally accepted that the ionic conductivity of SDC depends on the dopant type and concentration as well as the microstructure[38]. Since all the powders obtained in this study were from the same precursor and same composition, thus the synthesis method resulting in different microstructure/nanostructure must play a crucial role in ionic conductivity. The difference in nanodomain size is suggested to be another possible reason for the different conductivity values in this study and for those reported by others [6, 33, 36].

The co-sintering process has been applied in fabrication of anode-supported SOFCs since the anode with high shrinkage rate would facilitate the densification of the electrolyte [39, 40]. Figure 7 (a) shows the SEM images of the single cell sintered at 1200 °C. The Ni-GDC anode and LSCF-GDC cathode with thickness of around 500 μm and 25 μm were adhered well to the dense SDC electrolyte ($\sim 25 \mu\text{m}$). Figure 7 (b) shows the SEM view and enlarged view (inset) of the SDC electrolyte surface. No pores can be observable on the surface or cross-section, indicating that a highly dense SDC can be obtained by co-pressing the SDC-FC powder on the anode substrate and subsequently co-sintering at a temperature as low as 1200 °C.

Figure 7 (c) shows the cell voltage, current, and power density curves of cells at different operating temperature. The peak power density of the cell at 500, 550 and 600 °C were 0.111, 0.242 and 0.482 Wcm^{-2} , which were comparable with the one for cell using electrolyte from SDC-GNP powder and those for cells sintered at 1300 or 1350 °C[12, 41]. However, it is lower than the ones recently reported [14, 36]. In those reports, the SDC powder was prepared from a mixed precursors ($\text{Ce}(\text{NO}_3)_3$ and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$). All the materials including NiO anode, SDC electrolyte and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC)-SDC cathode were prepared by GNP method, while in our study commercially available NiO, GDC and LSCF were used. The difference in performance can be manifested by the electrochemical impedance spectra of the cell

measured at different temperatures, shown in Figure 7 (d). The ohmic resistance R_{Ω} , determined from the high frequency intercept of the impedance spectra with the real axis, is $0.118 \Omega\text{cm}^2$, while the polarization resistance R_p , obtained from the following equation (3) [42], is $0.664 \Omega\text{cm}^2$.

$$R_p = \frac{R_t - R_{\Omega}}{\frac{V_{OC}}{E_n} \left[1 - \frac{R_{\Omega}}{R_t} \left(1 - \frac{V_{OC}}{E_n} \right) \right]} \quad (3)$$

where R_t is the total resistance determined from the low frequency intercept with the real axis in the impedance spectra, R_{Ω} is the ohmic resistance, V_{OC} is the measured OCV, and E_n is the Nernst potential at 600°C .

The R_p is higher than those for the cell reported by Liu et al [14, 36]. The electrodes prepared from fine powders in those reports, especially cathode, are expected to show higher electrochemical reaction activity, thus resulting in lower interfacial polarization resistance.

4. Conclusion

In summary, nanocrystal-based macroporous powder has been fabricated by a solid freeze-drying combustion method. Taking SDC as an example, the average size of the 600°C -treated powder is 10-20 nm, with a surface area of $34.9 \text{ m}^2\text{g}^{-1}$. The powder shows better sinterability and higher conductivity. The nanodomain size in SDC-FC powder is in the range of 0.7-2 nm, smaller than the ones in powder by conventional liquid combustion. By co-pressing and co-sintering the SDC powder on anode substrate, a very dense electrolyte thin film can be achieved at a sintering temperature of 1200°C . This approach can be readily extended to produce large-scale nanoparticles of other single or mixed metal oxides.

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Figure 1 XRD pattern (a), powder SEM image (b), Bright Field TEM images (c) (Inset is the corresponding selected area electron diffraction (SAED) pattern) and High resolution TEM image (d) for SDC-FC powder heat-treated at 600 °C for 2 h.

Figure 2 Powder SEM and TEM images for SDC powder made through freeze-drying combustion (FC) (a-SEM, c-TEM) and glycine-nitrate process (GNP) (b-SEM, d-TEM)

Figure 3 HRTEM image for the SDC powder by freeze-drying combustion (a) and
GNP (b)

Figure 4 Surface SEM images for SDC pellets sintered at 1300 °C (a), 1350 °C (b), 1400 °C (c) (insets are the cross-sectional view of corresponding pellets) and dilatometric curves for the SDC bar prepared from different powder SDC-FC and SDC-GNP (d)

Figure 5 Cross-sectional SEM image for the SDC pellets made from freeze-drying combustion (FC) (a) and glycine-nitrate process (GNP) (b) sintered at 1400 °C for 5 h

Figure 6 Arrhenius plots of conductivity of SDC-FC pallets sintered at 1300, 1350 and 1400 °C

Figure 7 SEM image for the single cell (a), electrolyte SDC surface (b), I-V-P curve (c) and electrochemical impedance spectra (d) for cell when using H_2 as fuel and ambient air as oxidant