PREPARATION OF $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ SOLID ELECTROLYTE BY THE SOL-COMBUSTION METHOD

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ABSTRACT

$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) powders were prepared by a novel sol-combustion method using citric acid as the chelating reagent. The effects of different sintering temperatures were investigated on the evolution of crystalline phase, particle size, and lattice parameters of the resulted GDC powders. The results have shown that ultrafine GDC powders of around 40nm in diameter were successfully prepared by the sol-combustion technique. The powders showed a high sinterability, and a relative of 95.2% of the theoretical density was obtained at a sintering temperature of 1250°C. Electrochemistry measurements showed that the GDC ceramics had relatively high oxygen ionic conductivity in low-temperature range.

Keywords: SOFC; Doped CeO_2 ; Electrical conductivity; Sol-combustion method; Electrolyte

INTRODUCTION

Solid oxide fuel cell (SOFC) is a new chemical energy source with many advantages, such as transformation of chemical energy to electrical energy with high efficiency and low pollution to environment¹⁻³. Traditional solid oxide fuel cells based on yttria-stabilized zirconia (YSZ) can maintain sufficiently high ionic conductivity. However, the high operating temperature (above 1000°C) results in both higher costs and system degradation^{4,5}. Intermediate-temperature solid oxide fuel cells (IT-SOFCs) with an operating temperature of 500°C-600°C have been investigated by a number of researchers previously^{6,7}.

Ceria-based oxides have been suggested as one of the most promising electrolyte materials for IT-SOFCs. These materials show higher oxygen ionic conductivity at relatively lower temperature, compared with YSZ materials. Therefore, many studies have been carried out on ceria-based oxides doped with rare-earth elements, and many progresses have been made with regard to their properties as electrolytes for SOFC⁸⁻¹³.

Doped ceria oxide powders, such as $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{2-y}$, $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-y}$, $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-y}$, etc. ($y=0.5x$), have been prepared by the traditional solid-state reaction, in which oxide precursors were milled and calcined at a high temperature. The latter may cause the degradation of the electric and mechanical properties of the sintered bodies due to the impurity contamination¹⁴. Therefore, many soft-chemistry routes have been used to produce precursors at a lower temperature, as it is the case of fluorite precursors, to improve the preparation of ceria-based fluorite powders for IT-SOFCs application¹⁵⁻¹⁸.

In this study, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powders were synthesized by a sol-combustion method. Their sinterability and electrical conductivity were examined.

EXPERIMENTAL

Powder samples with the general formula of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) were synthesized by the sol-combustion method, as shown in Fig.1.

Fig.1. Flow chart of preparing $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powder by the sol-combustion process

Analytical pure cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, China National Medicines Corporation Ltd., China, containing CeO_2 39 wt.%), gadolinia (China National Medicines Corporation Ltd., China, 99.99wt.%), were used as starting materials. Cerium nitrate was dissolved in deionized water and the stoichiometric amount of gadolinia was dissolved in nitrate solution, then they were mixed together with citric acid solution (the mole ratio of cation to citric

acid was 1/1.5). The pH value of the system was adjusted to 7-8 with ammonia solution under continuous stirring at 40°C and a homogeneous sol was formed. The sol was then heated at 120°C for about 1h; a white alveolate precursor was obtained. The precursor was then calcined at different temperatures (650°C, 750°C, and 850°C) to get the final composition powders. The obtained powders were pressed into pellets under a pressure of about 200MPa, and then sintered at different temperatures (1000-1300°C) in air for 4h.

X-ray diffraction (XRD) analysis was performed with a rotating diffractometer (model: Rigaku-D/Max-γB, Rigaku, Japan) with the $\text{CuK}\alpha$ line ($\lambda=0.15406\text{nm}$), and the diffractograms were scanned in 2θ from 10° to 70° at a rate of 6°/min. The crystal size of the calcined powders was estimated using the Scherrer formula.

Ionic conductivity of the sintered GDC materials was measured on the sintered pellet samples. Silver paste was used as electrodes painted on both sides of each pellet. The measurement of AC impedance was performed in air with an electrochemical workstation CHI660B at a frequency range of 0.1Hz to 100 kHz. The measurement curves were conducted in the temperature range from 500°C to 800°C with an interval of 50°C.

RESULTS AND DISCUSSION

Phase structure

Fig.2 shows the X-ray diffraction patterns of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powders calcined at 650°C, 750°C, and 850°C. All diffraction peaks match well with ICDD PDF# 43-1002; no additional diffraction peaks were found, indicating that the substitution of Gd^{3+} ions into the Ce^{4+} sites took place.

Fig.2. XRD pattern of GDC powders calcined at different temperature

It can be seen that all samples were single phase with cubic fluorite structure; all the diffraction peaks can be attributed to 111, 200, 220, 311, 222, 400, 331 and 420 reflections of the single phase cubic structure of fluorite CeO_2 , and there were no other peaks of other phases. In the sol-gel process,

no other cations were added and the original cations did not lose, so the result material was pure production with a general formula $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$. This suggests that GDC powders with single phase can be successfully synthesized by the sol-combustion method by calcinations of the gel above 650°C, whereas ceria-based electrolytes prepared by conventional solid state reaction require calcinations temperatures around 1000°C. (at 650°C, 750°C, and 850°C).

The mean grain size of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ powders was calculated to be about 40nm based on Scherrer formula.

$$D = \frac{0.89\lambda}{B \cos \theta} \quad (1)$$

Where λ is the wavelength of X-ray, θ is the diffraction angle,

$B = \sqrt{Bm^2 - Bs^2}$ is the corrected halfwidth of the observed halfwidth: Bm is that of the (111) reflection in samples and Bs is that of the (111) reflection in a standard sample.

After heating at 650°C for 4h, the lattice parameter of the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ crystallized in a cubic fluorite structure is $a=0.54317\text{nm}$, which is slightly larger than that of the CeO_2 ($a=0.5411\text{nm}$). When Ce^{4+} ions of CeO_2 were partially substituted by Gd^{3+} ions, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ was formed. Though the ionic radius of Gd^{3+} (0.0938nm) is smaller than that of Ce^{4+} (0.1034nm), the substitution does not distort the structure of CeO_2 significantly, as shown by the similarity in the crystal lattice parameters, which are the same within the experimental error.

Sintering characteristics

Since the electrolyte must be gastight, it is said that an acceptable relative density of impervious ceramic electrolyte should be higher than 94%². Relative density of the sintered pellets was measured using the Archimedes method. Fig.3 shows the relative density of GDC ceramics sintered at different temperatures. The GDC powders showed a high sinterability; density of sintered GDC ceramics increases as sintering temperature increases, and a maximum relative density value (95.2%) of the theoretical one was obtained at sintering temperature of 1250°C, which satisfied the requirement for SOFC electrolytes operating at intermediate temperature range.

Fig.3. Dependence of relative density of GDC ceramics on sintering temperature.

Electrical conductivity

The ionic conductivity of sintered GDC samples was measured by AC impedance technique. The impedance spectra data were fitted with suitable equivalent circuit of the zsimpwin software to distinguish the bulk resistance from the grain-boundary resistance, and the conductivities were calculated. For a common ceramic electrolyte sample, the contributions to conductivity can be ascribed to the different conduction processes occurring in the bulk (a high-frequency semicircle originates in bulk conduction and dielectric processes), grain boundaries (an intermediate-frequency semicircle provides information on the grain-boundary and/or impurity contribution to ionic conduction), and electrode/electrolyte interfaces (a low-frequency semicircle or arc is generally due to ion and electron transfers at the sample surface contacting the electrode). The total resistance of electrolyte can be expressed as:

$$R = R_b + R_{gb} \quad (2)$$

where R_b is bulk resistance and R_{gb} is grain-boundary resistance. Therefore, the total resistance of the electrolyte can be obtained from the spectra and converted to a conductivity datum σ , using the relation.

$$\sigma = \frac{L}{R \cdot S} \quad (3)$$

where L is the sample thickness and S is the electrode area on the sample surface. These parameters are compiled in Table1. With the increase of the operating temperature, the total resistance decreases, and the electrical conductivity datum, σ , increases. The conductivity of GDC sintered at 1250°C for 4h in air reached $7.64 \times 10^{-2} \text{S} \cdot \text{cm}^{-1}$ under the testing temperature of 800°C.

Table1 Electrical conductivity of GDC sample at different testing temperatures.

Testing temperature (°C)	500	550	600	650	700	750	800
Electrical conductivity, σ ($\text{S} \cdot \text{cm}^{-1}$)	4.55×10^{-3}	8.37×10^{-3}	1.34×10^{-2}	2.86×10^{-2}	4.09×10^{-2}	5.82×10^{-2}	7.64×10^{-2}

The conductivity data were analyzed further using the Arrhenius equation.

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{E}{kT}\right) \quad (4)$$

where E is activation energy of electrical conduction, k is the Boltzmann constant, T is the absolute temperature and σ_0 is a pre-exponential factor, being constant in a certain temperature range. Fig.4 shows the Arrhenius plots of the electrical conductivity for the sample sintered at 1250°C at the temperature range from 500°C to 800°C. The activation energy of the total conductivity for the sample sintered at 1250°C was estimated to be 0.87eV.

Fig.4. Electrical conductivity of GDC sample sintered at 1250°C in air

Fig.5 shows the Arrhenius plots of the electrical conductivity for the GDC samples treated after different sintering temperatures at various testing temperatures. It can be seen from Fig.5 that the electrical conductivities of the GDC samples for a given testing temperature increased as sintering temperature increased up to 1250°C, while the total electrical conductivities of the samples sintered at 1300°C and 1250°C are almost the same. This phenomenon means that the pellets were dense when sintered up to 1250°C. However, when sintered beyond 1250°C, grain size of GDC samples grew rapidly to form coarse and big grains, and at the same time, more and larger pores appeared. Thus, the

density of the pellets began to increase much more slowly. So the electrical conductivity of the sample sintered at 1300°C was similar to or not much higher than that of the sample sintered at 1250°C. The reason may be that the lattice oxygen loss of this system at high temperatures caused the decrease of electrical conductivity due to the reduction of charge carrier concentration¹⁹.

Fig.5. Total electrical conductivity obtained for GDC samples sintered at different temperatures.

CONCLUSIONS

Nanosized $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) powders were prepared by a new sol-combustion method. When calcined over 650°C, the sample presents a single phase with cubic fluorite structure. At sintering temperatures higher than 1250°C, the sintered pellet samples become denser much more slowly than below that temperature. The sample sintered at 1250°C showed relatively high electrical conductivity and low activation energy as electrolytes in the intermediate-temperature SOFC. The conductivity of GDC sintered at 1250°C and tested at 800°C can reach $7.64 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$; the activation energy of the total conductivity for the sample was 0.87 eV.

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