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Preparation and properties of rare earth co-doped $Ce_{0.8}Sm_{0.2-x}Y_xO_{1.9}$ electrolyte materials for SOFC

Xueqing Sha [a], Zhe Lü [a], Xiqiang Huang [a], Jipeng Miao [a], Li Jia [b], Xianshuang Xin [a], Wenhui Su [a,b,c,d,*]

[a] *Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, China*
[b] *Department of Physics, Dalian University of Technology, Dalian 116024, China*
[c] *Department of Condensed Matter Physics, Jilin University, Changchun 130023, China*
[d] *International Center for Materials Physics, Academia Sinica, Shenyang 110015, China*

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Abstract

Ceria-rare earth solid solutions are known as solid electrolytes with potential applications in solid oxide fuel cell (SOFC). Trivalent rare earth ions enter into solid solution introducing anion vacancies for charge compensation. These oxygen vacancies are quite mobile at moderate temperatures giving rise to a comparatively high ionic conduction. In this study, rare-earth co-doped $Ce_{0.8}Sm_{0.2-x}Y_xO_{1.9}$ ($x = 0.0$–0.20) fine powders were prepared by a sol–gel method. The XRD results showed that all powders crystallite calcined at 800 °C were single phase with cubic fluorite structure; the average crystallite size was between 24 and 35 nm, which was in good agreement with the results of TEM and particle size distribution measurements. The SEM results exhibited that electrolyte pellets sintered at 1400 °C were dense, and the relative densities of these pellets were over 99%. Impedance spectra analysis of these electrolytes has been performed at 250–850 °C. The results displayed that $Ce_{0.8}Sm_{0.15}Y_{0.05}O_{1.9}$ and $Ce_{0.8}Sm_{0.1}Y_{0.1}O_{1.9}$ appeared higher conductivity and lower activation energy than the singly doped ceria with the same dopant concentration (20% trivalent rare earth) at the temperature range of 550–700 °C. The maximum power density and the maximum current density for the single SOFC based on the two samples were higher than singly doped sample with the same vacancy concentration. Therefore, it is concluded that co-doping with an appropriate ratio of samarium and yttrium can further improve the electrical performance of ceria-based electrolytes.

Keywords: SOFC; Co-doped; Ceria; Electrolyte

1. Introduction

Solid oxide fuel cell (SOFC) has attracted much attention in recent years because of its high-energy conversion efficiency and environmental friendship. It is widely considered to be a new clean power source for current century. By far, the most extensively studied electrolyte material is yttria-stabilized zirconia (YSZ). SOFCs with YSZ as oxygen ionic conductor must operate above 800 °C to get satisfactory power output. However, such high temperatures often lead to some problems such as solid reactions between the components, thermal degradation and thermal expansion mismatch. It becomes increasingly important to reduce the operating temperature of the SOFCs. Therefore, great efforts have been made to reduce the operating temperature. One effective approach is adapting doped ceria electrolytes that exhibit superior ionic conductivity at lower temperature range (600–800 °C) [1–3].

So far, ceria-based electrolytes have been extensively studied and made much progress [4–15]. Some singly doped electrolytes, such as $Ce_{1-x}Sm_xO_{2-y}$ (SDC), $Ce_{1-x}Gd_xO_{2-y}$ (GDC) and $Ce_{1-x}Y_xO_{2-y}$ (YDC), etc., show high oxide ion conductivity, but the SOFCs based on those have not met the commercial requirement up to now. With the purpose of further optimize electrolyte, co-doping method has been used in resent years and was proved to be effective. Many co-doped ceria-based electrolytes have been investigated, such as $Ce_{1-x-y}Sm_xCa_yO_{2-z}$, $Ce_{1-x-y}La_xSr_yO_{2-z}$ [16], $Ce_{1-x-y}Gd_xPr_yO_{2-z}$ [17], $Ce_{0.85}Gd_{0.1}Mg_{0.05}O_{1.9}$ [18], $Sm_xGa_{0.2-x}Ce_{0.8}O_{1.9}$ [19] and so on. However, to the best of our knowledge, no studies are reported on samaria and yttria

* Corresponding author. Tel.: +86 451 86418570; fax: +86 451 86412828.
E-mail address: suwenhui@hit.edu.cn (W. Su).

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co-doped ceria. Considering the higher oxide-ion conductivity of SDC and YDC in doped ceria, Sm and Y co-doped ceria electrolytes were prepared by the sol–gel method, and their crystal structure, thermal expansion, electrical conductivity were characterized and compared in this study. The aims were to develop new ceria-based electrolyte materials to further improve the ionic conductivity and to conduct the initial tests with single cells.

2. Experiment

2.1. Sample preparation

A series of solid solution with the general formula of $Ce_{0.8}Sm_{0.2-x}Y_xO_{1.9}$ ($x = 0$, 0.05, 0.10, 0.15 and 0.20) were synthesized by the sol–gel method. Cerium nitrate (CeO2, 39 wt.%), yttria, and samaria (99.5 wt.%) are used as starting materials. Cerium nitrate was dissolved in deionized water and the desired amounts of yttria and samaria were dissolved nitrate solution, then they were mixed together with citric acid solution. The pH value of the mixed solution was adjusted with ammonia solution under continuous stirring at 70 °C and homogeneous sol was formed. With the evaporation of water, a yellow sponge-like gel was obtained, then the gel was placed in a 80 °C drying oven, where the gel occurred self-igniting reaction and became light yellow powder, which was ground and calcined at 200, 400, 600 and 800 °C in air for 2 h, respectively.

The dried powders were ground in an agate mortar and then pressed under a pressure of about 200 MPa into cylindrical pellets (13 mm in diameter and 0.6 mm in thickness). The pellets sintered at 1400 °C and 1450 °C in air for 10 and 9 h, respectively.

2.2. Property measurement

The crystal structure of the calcined oxide powders and pellets were determined by X-ray diffraction (XRD) analysis using a Bede D1 X-ray Diffractometer (monochromated Cu Kα radiation, $\lambda = 0.15418$ nm; operated at 40 kV, 45 mA) at room temperature, in the Bragg angle range of $20° \leqq 2\theta \leqq 80°$. The crystallite size, D, of the calcined powders was estimated using the Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Cell parameters were calculated by fitting the observed reflections with a least-squares program. The density of the sintered pellets was determined by the Archimedes method and expressed as relative to the theoretical values determined by the XRD cubic lattice parameters. Particle size distribution was performed using a Malvern Mastersizer2000 laser particle size analyzer. Transmission electron microscopy (TEM) examination of the samples was carried out with a JEOL JEM-1200EX electron microscope working at 100 kV. The samples were dispersed in ethanol by sonication and dropped on a conventional carbon-coated copper grid. Scanning electron microscopy (SEM) micrographs were taken on the broken faces of the specimens using a Hitachi S-570 scanning electron microscope. Thermal expansion measurements were conducted with a Netzsch DIL 402C/3/G dilatometer in air, operated from 50 to 900 °C (heating rate 5 °C min^{-1}, flow rate 50 ml min^{-1}).

2.3. Electrical measurement

The electrical conductivity of the materials was measured based on the sintered ceramic pellets. Silver paste (DAD-87 type) was used as electrodes on opposite sides of each tablet. The complex impedance spectra of the pellets were measured using a computerized Solartron SI1260 Impedance Analyzer combination with a Solartron SI1287 electrochemical interface (EI).

The measurements were conducted in air in the temperature range from 250 to 850 °C and in the frequency range from 0.5 to 910 kHz. The measured resistance data was corrected by measuring the area of the electrodes and the thickness of the samples. The impedance spectra data was analyzed using the Equivalent Circuit of the Z-View 2.0 software.

2.4. Fuel cell fabrication and test

Single cells were constructed based on the electrolyte pellets. The mixed powder of NiO (70 wt.%)-$Ce_{0.8}Sm_{0.2-x}Y_xO_{1.9}$ were added glycerol to make a slurry, then the slurry was painted on one side of a pellet as the anode, which was sintered at 1200 °C for 2 h. The mixture of $Sm_{0.5}Sr_{0.5}CoO_3$-Ag (20 wt.%) [20] were added terpineol to make a slurry. The slurry was sprayed on the other side of the pellet as the cathode. The sandwich structure was sintered at 940 °C for 3 h. Silver wires were attached on both anode and cathode as leaders with DAD-87 paste. The SOFCs were tested in a tube furnace at temperatures from 550 to 800 °C. Ambient air was maintained on the cathode side. At the start of each test, H_2 with about 3% H_2O flowed through the anode compartment with the cell at 700 °C for 0.5 h to reduce the NiO in anode to Ni.

3. Results and discussion

3.1. Phase structure

Fig. 1 shows the X-ray diffraction patterns of the SDC powders heat-treated at various temperatures. It can be seen that all powders crystallite were single phase with cubic fluorite structure. The width of the XRD peaks gradually decreases with the calcined temperature increasing. The corresponding crystalline particle sizes determined from the Scherrer equation for the calcined powders are growing from 11.5 nm (200 °C) to 28 nm (800 °C).

Fig. 2 displays the X-ray diffraction patterns of the $Ce_{0.8}Sm_{0.2-x}Y_xO_{1.9}$ powders calcined at 800 °C. It was found that the doped ceria powders crystallite are single phase with cubic fluorite structure, which was the same as the original substance of pure ceria. The average crystallite sizes of the sample powders calculated by the Scherrer formula, are between 24 and 35 nm.

Cell parameters were calculated by fitting the observed XRD reflections of the five samples sintered at 1450 °C and the dependence of unit cell parameter versus dopant concentration is shown in Fig. 3. As can be seen, the unit cell parameter decrease

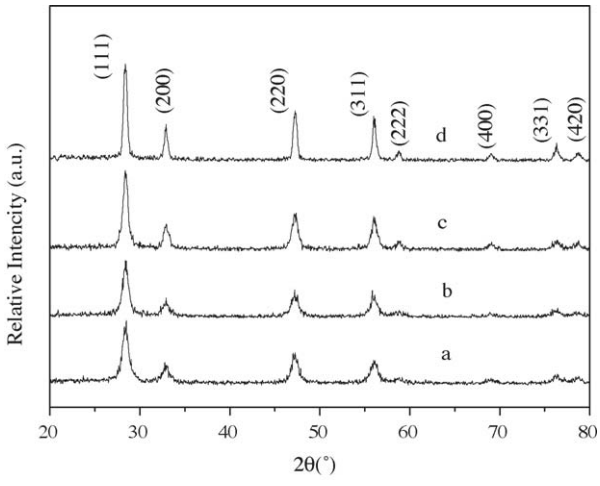

Fig. 1. X-ray diffraction patterns of SDC powders calcined at various temperatures: (a) 200 °C; (b) 400 °C; (c) 600 °C; (d) 800 °C.