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Synthesis and Characterization of Samarium-Doped CeO_2 Powders as a Solid Electrolyte by Using Pechini Method

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In the trivalent rare-earth doped ceria electrolyte for SOFC applications, the highest conductivities are observed for $Ce_{1-x}Sm_xO_{2-x/2}$ and $Ce_{1-x}Gd_xO_{2-x/2}$. In this study, fully dense samarium doped ceria ceramics (SDC), $Sm_xCe_{1-x}O_{2-x/2}$ ($x = 0.1$) have been synthesized via Pechini method. The phase identification, microstructural properties and bond structure of SDC samples were studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform- Infrared Spectroscopy (FTIR). The XRD results indicate that a single-phase fluorite structure has formed at relatively low calcination temperature of 500 °C. This method yields high purity ultrafine powders which can form dense electrolyte at relatively low sintering temperatures. The SEM results show that a complete solid solution between ceria and samarium was obtained at the sintering temperature of 1400 °C.

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1. Introduction

Solid oxide fuel cells (SOFCs) have a great potential to be the cleanest, most efficient, and versatile material for the chemical-to-electrical energy conversion. SOFCs have the advantage of fuel flexibility, and the capability of working with hydrogen, hydrocarbon reformate and, in some circumstances, directly with hydrocarbon fuels [1]. In general, traditional SOFC systems use yttria-stabilized zirconia (YSZ) as the electrolyte material [2, 3]. This typical material requires a high operation temperature (1000 °C). Such a high operation temperature introduces many practical problems, such as high costs, materials degradation, thermal expansion mismatch, reactions between the cell components, slow start-up and shut-off, etc. [4, 5]. It is thus necessary to lower the operating temperature of the SOFCs. Ceria doped with alkaline earth oxides or rare earth oxides, has been considered as one of the most promising candidate materials for low operating temperature SOFCs because of its much higher ionic conductivity at lower temperatures in comparison with that of stabilized zirconia. The ionic conductivity of ceria increases significantly with the oxygen vacancies created by the doping of rare earth cations into the ceria lattice. The ionic conductivity at 750 °C of doped ceria is similar to that of YSZ at 1000 °C [6–8]. Among the various dopants used, Sm^{3+}, Dy^{3+}, and Gd^{3+} are favorable for increasing the ionic conductivity [6, 7, 9]. To obtain the ceria based electrolyte materials, various techniques have been used such as sol–gel, combustion, mechanochemical and homogeneous precipitation [10–13].

In this study, high purity cerium and samarium salts were used to form ceria-based solid solution through the Pechini method. Crystal structure and microstructure were characterized by means of XRD and SEM. Moreover, bond characterization of the SDC samples was performed by using Fourier Transform Infrared Spectroscopy (FT-IR) technique. The ionic conductivity of ceria doped with samarium was also determined via electrochemical impedance spectroscopy as a function of temperature by using A.C. impedance spectroscopy in air.

2. Experimental Procedure

2.1. SDC Preparation

Cerium (III) nitrate hexahydrate ($Ce(NO_3)\cdot 6H_2O$, 99.9%, Aldrich), samarium (III) nitrate hexahydrate ($Sm(NO_3)\cdot 6H_2O$, 99.9%, Aldrich) were used as metal precursors and ethylene glycol (R.P. Normopur), citric acid (Boehringer Ingelheim) were selected for the polymerization treatment. $Ce_{0.9}Sm_{0.1}O_{1.95}$ was synthesized by the Pechini method. More details about the Pechini method are reported in our earlier work [14].

2.2. Powder Characterization

XRD technique was used to determine the crystal structure and phase purity. The X-ray spectra of samarium-doped ceria particles were obtained over the 2θ range of 10–90° by using Rigaku D/max-2200 PC X-ray diffractometer with Cu-Kα radiation at a scan of 2 °/min. The calcined powders were pressed into a disk at 200 MPa with CIP. The compact disk of SDC powders was then sintered at 1400 °C for 6 h with a heating rate of 5 °C/min. The densities of the sintered discs (D_{pellet}) were determined by using the well- known Archimedes's method (Eq. 1):

$$D_{\text{pellet}} = W\rho/W1 - W2, \quad (1)$$

where W is the dry weight, W_1 is the wet weight (water

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in body), W_2 is the body's submerged weight without fine wire and ρ is the density of the solvent (water at 25 °C, 0.997 $g cm^{-3}$). The value of theoretical density (D_{th}) was calculated as 7.16 $g cm^{-3}$.

The structural features of the gel SDC precursor (dried at 110 °C) and reactants were characterized by Perkin-Elmer FT-IR (Spectrum 100) spectroscopy using KBr pellet method in the range of 400–4000 cm^{-1}. The microstructure of the sintered samples was characterized by means of SEM using FEI Quanta FEG 450 microscope. The ionic conductivity measurements of the sintered pellets were obtained with an AC impedance analyzer (Solartron 1260 FRA and 1296 interface) in the temperature range of 250–550 °C in air atmosphere.

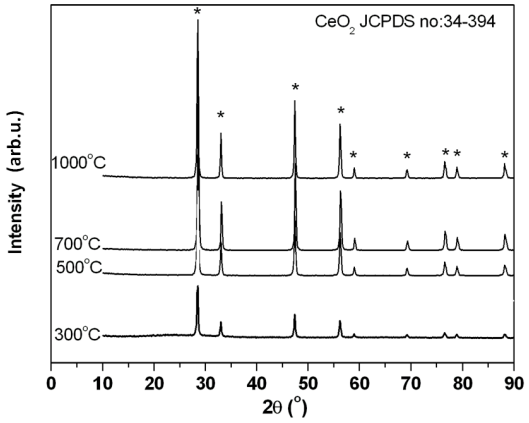

Fig. 1. XRD patterns of the SDC powders calcined at 300, 500, 700 and 1000 °C, 2 h.

3. Results and Discussion

3.1. X-ray Analysis

The XRD patterns for the SDC powders are shown in Fig. 1. According to the results of XRD, all powders had a single-phase fluorite structure, even when calcined at 300 °C. It can be clearly seen that characteristic diffraction peaks related to fluorite-like structure were around 300 °C. This indicates that a relatively low calcination temperature is needed to prepare SDC powders by the Pechini method. The crystallite size of the powders calcined at 300 °C is 10.8 nm. These peaks gradually sharpen with increasing heat treatment temperature, which indicates the increase of the crystallite size. The samarium oxide was not detected. The results indicate that the dopant ion was fully substituted in the CeO_2 lattice.

3.2. FT-IR Analysis

To obtain a better insight into the reaction at the pyrolysis process, FT-IR spectra were obtained for chemical precursors at various calcinated temperatures. Figure 2 displays the FT-IR spectra for the SDC precursors dried at 110 °C and after the calcination at 700 °C. The broad peak in the range of 3000-3700 cm^{-1} represents hydroxyl groups (O–H). Other vibrations are

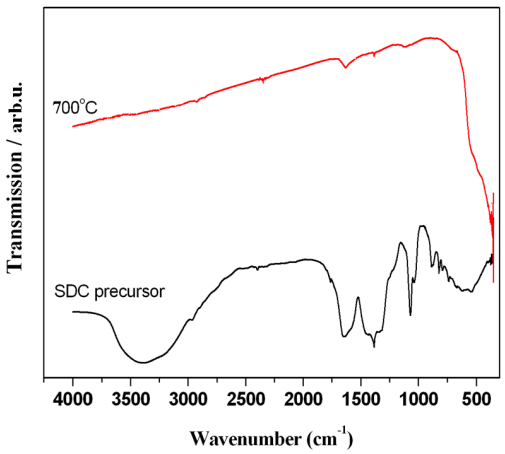

Fig. 2. FT-IR spectra of SDC precursors heat-treated at 110 and 700 °C.

as follows: CH_2 stretching (2920 cm^{-1}), C=O vibration (1540 cm^{-1}), COO^- vibration (1430 cm^{-1}), COO^- stretching (1380 cm^{-1}) and C–O stretching (1080 cm^{-1} and 1040 cm^{-1}).

In the spectrum of the specimen dried at 110 °C, most of the infrared bands found in the dried precursor are observed. The intense band detected in the range of 3000–3700 cm^{-1} is attributed to O–H stretching of physically absorbed H_2O or surface –OH group. And also, the C=O and C–O vibration (around 1540 and 1430 cm^{-1}) can still be seen from the spectrum, indicating that the nitrates and other organic compounds did not yet decomposed at this temperature [15]. It can be clearly seen that when the temperature reached to 700 °C, the bands of CO group almost disappeared. After calcination at 700 °C, the broad and high absorption band at the range from 500 cm^{-1} to 700 cm^{-1} could be attributed to metal–oxygen band, which indicates the formation of the samarium doped ceria (SDC).

3.3. SEM Results

Figure 3 shows SEM micrographs of the sintered at 1400 °C SDC samples, prepared from powders calcined at 1000 °C.

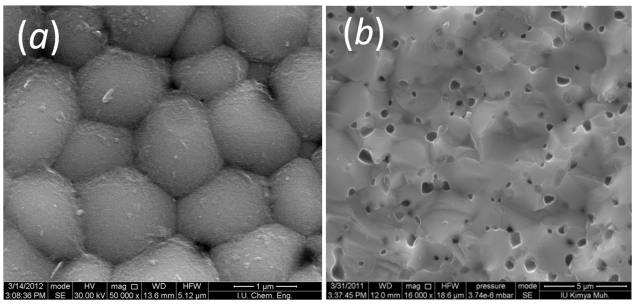

Fig. 3. SEM of the sintered pellets of SDC at 1400 °C for 6 h, (a) the surface of SDC pellet, (b) cross-sectional fracture surfaces of SDC samples.

The sintered bodies at 1400 °C had dense structures (97.6% of the theoretical density) and a very little porosity was observed (Fig. 3a and 3b).

It demonstrates the high sintering activity of SDC powders prepared by the Pechini process. These samples have fully dense structure with relatively small volume of grain boundary. Therefore the dense $Sm_{0.1}Ce_{0.9}O_{1.95}$ pellet sintered at 1400 °C had good total conductivity value.

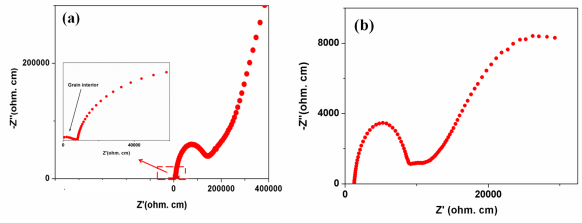

Fig. 4. Impedance spectra of the SDC pellets sintered at 1400 °C for 6 h, recorded at (a) 300 °C and (b) 400 °C.

3.4. Conductivity Results

The complex impedance spectra of SDC pellets measured at 300 and 400 °C in air atmosphere are seen in Fig. 4. The impedance spectra represent resistivity of internal grain and grain-boundary from half-circle in two regions. In Fig. 4a, there are two semicircular arcs, which denote the grain interior and grain boundary. While the grain interior arc (the first half-circle in left side) is not clearly recognized, the grain boundary arc is discernible. With increasing temperature (fig. 4b), the first half-circle (the high-frequency arc) disappears and only the grain boundary and electrode arcs are visible. It is understood from the impedance curves that grain boundary conductivity (R_{Gi}) effect becomes more dominant on the overall conductivity (R_T) value of SDC ceramics. With increasing operating temperature from 300 to 400 °C, the resistivity of grain boundary decreases. In other words, at high temperature a single half-circle can be seen and the total resistance is found to be decreasing with increasing operating temperature.

4. Conclusions

The Pechini method enables working at low synthesis temperatures and it requires a modest experimental equipment. After the calcination process at about 300 °C main peaks of ceria (CeO_2) structure was observed from XRD curve. A single fluorite phase is obtained. The XRD results indicate that a relatively low calcination temperature is needed to prepare SDC powders by the Pechini method. After sintering for 6 h, the samarium-doped ceria pellets achieved 97.6% of the theoretical density at 1400 °C. According to the electrochemical impedance spectroscopy results, SDC exhibited a total conductivity of 4.83×10^{-4} S cm^{-1} at 550 °C in air. Phase purity, stability and relative density are the important factors for obtaining high performance SDC electrolytes. Therefore, the Pechini method is a promising candidate for the preparation of SDC electrolytes.

Acknowledgments

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