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Structural and electrical properties of $Ce_{0.75}(Gd_{0.95-x}Sr_xCa_{0.05})_{0.25}O_{2-\delta}$ thick film electrolyte

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ABSTRACT

The effects of Sr doping on the electrical properties of $Ce_{0.75}(Gd_{0.95-x}Sr_xCa_{0.05})_{0.25}O_{2-\delta}$ ($x = 0, 0.01, 0.02, 0.03, 0.04, 0.05$ mol%) electrolytes thick films were investigated. The samples sintered at 1400 °C for 8 h. X-ray diffraction (XRD) showed typical XRD patterns of a cubic fluorite structure, and the ionic conductivity was examined by AC impedance spectroscopy. From the experimental results, it was observed that $Ce_{0.75}(Gd_{0.95-x}Sr_xCa_{0.05})_{0.25}O_{2-\delta}$ ($x = 0.04$ mol%) electrolytes thick film have higher conductivity and minimum activation energy at 600 °C. This is explained in terms of the increased in the oxygen vacancy concentration at the grain boundary.

1. Introduction

As energy generation devices are developed, solid-oxide fuel cells (SOFCs) can now convert chemical energy into electrical energy while retaining both environmentally friendly and fuel-flexible characteristics. Typical SOFCs based on the yttria-stabilized zirconia (YSZ) electrolyte have a high operating temperature range in general (800–1000 °C) and can therefore obtain a high ionic conductivity. The high operating temperature causes numerous problems, such as a high fabrication cost and the degradation of the cell components [1,2]. In order to solve these problems, Ce is the most suitable material to use at low-intermediate temperatures (500–700 °C), and research in this area based the on doped ceria electrolyte attracts much attention. The ionic conductivities as well as diverse properties of ceria-based electrolytes doped with various dopants (e.g., Sm^{3+}, Gd^{3+}, $Y3^{+}$, and Ca^{2+}) have been studied. Among the various dopants, Sm- or Gd-doped ceria reportedly has the highest conductivity. However, due to the high sintering temperature, these dopants are difficult to densify below 1500 °C, and the reduction of Ce(IV) to Ce(III) occurs. It has been reported that a reduction of ceria can be ignored at lower temperatures. In order to more enhance the electrical properties of singly doped ceria, co-doped ceria has been considered as one of the most promising electrolyte materials for IT-SOFCs [3,4]. Aliovalent dopants such as rare earths and alkaline earths' cations form solid solutions with ceria and introduce vacancies in the anion sub-lattice as charge-compensating defects. Oxygen ion vacancies are responsible for the ionic conductivity observed in doped ceria [3]. Co-doping ceria with alkaline earth and rare earth ion materials offers higher conductivity and lower activation energy than undoped ceria. Some alkaline earth elements act as scavengers that are resistant to siliceous impurity phases in the grain boundaries. In particular MgO, CaO, SrO and BaO are effective with Gd-doped ceria [5–8]. In addition, the ionic radius of Sr^{2+} (0.126 nm) is larger than that of Ce^{4+} (0.097 nm). It is expected that the ionic conductivity will be enhanced by the substitution of Sr^{2+} ions because the microstructure of the space-charge layer near the grain boundary may be optimized. An electrolytes thick film process to create larger films requires a vacuum-deposition process with a lower sintering temperature. In this paper, the effects of Sr as a co-dopant on the properties of ceria-based electrolyte materials and the microstructures as well as the electrical properties are investigated.

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2. Experiments

High-purity powders of CeO_2, $CaCO_3$, Gd_2O_3, and $SrCO_3$ were mixed and ground with ethanol in a ball mill. After being dried at 100 °C for 24 h, the powder was calcined at 1100 °C for 3 h. The resultant powders were again ball-milled into a fine powder. Screen-printable pastes were prepared by kneading in the ground powder with 30 wt% of an organic vehicle (Ferro B75001) in a non-bubbling kneader (NBK-1, Kyoto Electro). High-purity alumina was used as a substrate. The bottom electrodes were prepared by screen printing with Pt paste and were fired at 1450 °C for 20 min After screen printing the $Ce_{0.75}(Gd_{0.95-x}Sr_xCa_{0.05})_{0.25}O_{2-\delta}$ pastes using a 325 mesh screen mask, the printed films were allowed to level for 10 min and were then dried at 80 °C for 30 min The electrolytes thick films were sintered at 1400 °C for 8 h with an intermediate 2 h isothermal at 600 °C to remove the organic components. The upper electrodes were fabricated by screen printing with Ag paste and were then fired at 400 °C for 10 min. Each sample was heated in small tube furnace individually to impedance measurement at different temperature and two point probe of impedance analyzer was connected electrode of samples in small tube furnace.

The crystal structures of the samples were analyzed by X-ray diffraction (XRD) and the microstructures of the samples were measured using a scanning electron microscope (SEM). The impedance spectra of the samples were measured using an impedance analyzer (HP4194A). The measuring frequency range was between 10 Hz and 40 MHz, and the temperature ranged from 400 °C to 800 °C. Agilent IO control software was used to analyze the impedance data and to calculate the conductivity of the samples.

3. Results and discussion

Fig. 1 shows the temperature-dependent X-ray diffraction patterns of the $Ce_{0.75}(Gd_{0.95-x}Sr_xCa_{0.05})_{0.25}O_{2-\delta}$ ($0 \leq x \leq 0.05$ mol%) mol%) electrolytes thick film. Pellets were sintered at 1400 °C. We observed that no phase transition appears between $0 \leq x \leq 0.05$ mol%. It was also noted that all samples had a single phase with a cubic fluorite structure such as pure CeO_2. According to Bragg's Law, $n\lambda = 2d\sin\theta$, the value of d is increased with a shift of θ to a lower degree. The 2θ values of the Sr-doped ceria shift slightly toward lower angles as x changes from 0 mol% to 0.5 mol%. As follows, the ionic radius Ce^{4+}(0.097 nm), Gd^{3+}(0.1053 nm), Ca^{2+}(0.112 nm), and Sr^{2+}(0.126 nm). The relationship between the lattice parameter and the Sr content is shown in Fig. 2.

$$a = d\sqrt{h^2 + k^2 + l^2} \qquad (1)$$

Here, 'a' is the lattice parameter, and as Sr content increases, the lattice parameter linearly increases. This is why the Sr^{2+}(0.126 nm) sample has a much larger ionic radii size compared to other ions. The substitution of Sr^{2+} in the CeO_2 lattice caused strain in the lattice; as a result the diffraction peaks shift.

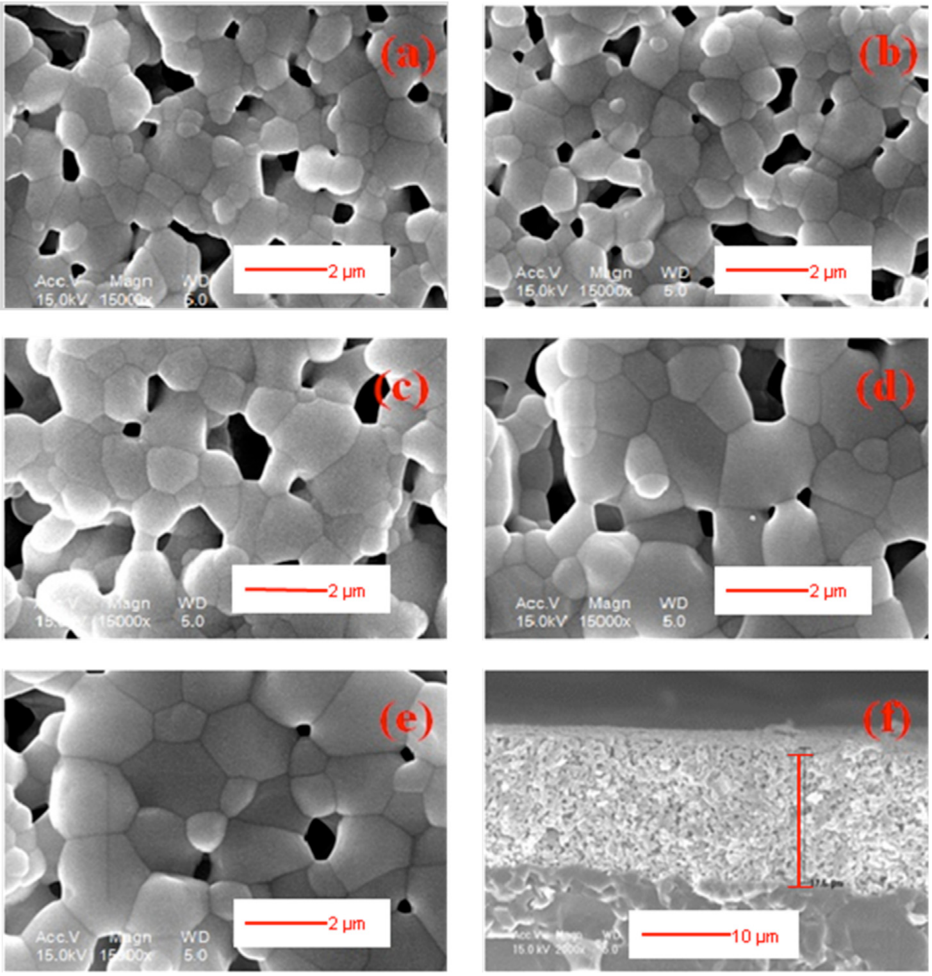

Fig. 1. X-ray diffraction patterns of $Ce_{0.75}(Gd_{0.95-x}Sr_xCa_{0.05})_{0.25}O_{2-\delta}$ ($0 \leq x \leq 0.05$ mol%) electrolytes thick films.