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# Electrical and structural properties of $Ce_{0.8}(Sm_{0.5-x}Y_{0.5}Al_x)_{0.2}O_{2-\delta}$ ceramics as an electrolyte for SOFC

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ABSTRACT

The effects of various contents of alumina co-doping on a ceria-based electrolyte were investigated. All samples were sintered at 1500 °C for 10 h. The X-ray diffraction (XRD) patterns showed a fluorite cubic structure. To investigate the surfaces of the $Ce_{0.8}(Sm_{0.5-x}Y_{0.5}Al_x)_{0.2}O_{2-\delta}$ (CSYA) ceramics by scanning electron microscopy (SEM), the electrical properties of the CSYA ceramics were measured by AC impedance. The optimal values of ionic conductivity and activation energy were reached at $x = 0.4$ measured at 600 °C. This result indicated that the alumina co-doping improved the electrical and microstructural properties of the ceria-based electrolyte.

## 1. Introduction

Renewable energy systems are receiving worldwide attention due to the inevitable exhaustion of fossil fuels, and researchers are attempting to improve the performance of renewable energy systems [1,2]. Of the many areas of research, the solid oxide fuel cell (SOFC) has been extensively studied because of its advantages, including high energy conversion, low environmental pollution and sustainable energy production. Yttria-stabilized zirconia (YSZ) has been widely used in various fields because of its high ionic conductivity, chemical stability and low thermal expansion coefficient [3,4] which also make it attractive for use in SOFCs. However, the YSZ has disadvantages, such as thermal expansion mismatch and long set-up time due to its high operating temperature (~1000 °C). As mentioned above, The SOFC having a low operating temperature (500–700 °C) is required, such as an intermediate temperature SOFC (IT-SOFC) [5,6]. As potential alternatives to the YSZ, many replacement materials have been studied. Among these, the ceria based electrolyte was found to have superior electrical properties, such as high ionic conductivity, low operating temperature and good compatibility with electrodes [7–10].

In order to improve its ionic conductivity further, researchers have doped ceria-based electrolytes with various rare earths and alkaline earth dopants ($Ca^{2+}$, $Sm^{3+}$, $Gd^{3+}$, $Y^{3+}$ and $La^{3+}$) [11]. When doped, these ceria electrolytes have shown high ionic conductivity, but are not suitable for commercial and general application. Moreover, $Ce^{4+}$ tends to be reduced to $Ce^{3+}$ because of the high sintering temperature requirement, and reduced ceria is not useful at low temperature (600–700 °C). In order to further enhance the electrical and micro structural properties of single-dopant electrolytes, co-doping of ceria has been investigated. The co-doped ceria electrolytes were found to be the optimal electrolyte materials for the IT-SOFC. Many co-doping materials have been studied, such as the rare earth metals, alkaline earths' cations and transition metals. The co-doping materials lower the sintering temperature, introduce oxygen vacancies, lower the activation energy and increase the ionic conductivity [12–17].

In this paper, we investigated the effect of various contents of yttria and alumina on ceria-based electrolytes, and the effect of yttria and alumina content on structural and electrical properties.

## 2. Experiments

La doped $Ce_{0.8}(Sm_{0.5-x}Y_{0.5}Al_x)_{0.2}O_{2-\delta}$ (CSYA) ceramics were fabricated by a conventional solid-state reaction method. High purity powders of $CeO_2$ (99.9%, Kanto chemical Co.), $Sm_2O_3$ (99.9%, Aldrich Co.), $Y_2O_3$ (99.9%, Aldrich Co.) and $Al_2O_3$ (99%, Aldrich Co.) were mixed and ground with ethanol in a ball mill for 24 h. After drying at 100 °C for 24 h, the powder was calcined at 1100 °C for 3 h in air. After drying at 100 °C for 24 h, the powder was calcined at 1100 °C for 4 h. The calcined powders were pressed into disk samples of 12 mm diameter. The samples were sintered at 1500 °C for 10 h and then were polished to 1.0 mm thickness. Silver paste was screen-printed on the surfaces for electrodes and then fired at 400 °C for 10 min. The crystal structures of the samples were analyzed by the X-ray diffraction (XRD) and the microstructures of

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the samples were measured using the scanning electron microscopy (SEM). The impedance spectra of the samples were measured using an impedance analyzer (HP4194A). The measurement frequency range was between 10 Hz and 40 MHz, and the temperature ranged from 400 °C to 800 °C in air. 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 X-ray diffraction patterns of the $Ce_{0.8}(Sm_{0.5-x}Y_{0.5}Al_x)_{0.2}O_{2-\delta}$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5) ceramics with various Al contents. All patterns show a single phase with a fluorite cubic structure and no secondary phase, suggesting that $Al^{3+}$ ions can be well substituted into the ceria lattice. From Bragg's law, $n\lambda = 2d\sin\theta$, where $n$ is an integer determined by the order given, $\lambda$ is the wavelength of X-ray, $d$ is the spacing between the planes in the structure and $\theta$ is the angle between the incident ray and the scattering planes. When the Al content was increased up to 0.5, the $2\theta$ value of CSYA shifted slightly towards the upper degree because the value of $d$ was decreased; on the other hand, the degree of $\theta$ was increased. The correlation between the lattice constants and the various contents of Al is shown in Fig. 2. As shown, the lattice constants linearly decreased with increasing Al content because the ionic radius of $Al^{3+}$ (0.5 Å) is smaller than the ionic radius of the other ions such as $Ce^{4+}$ (0.97 Å), $Sm^{3+}$ (0.96 Å) and $Y^{3+}$ (0.93 Å), respectively. As a result of the above, it was confirmed that $Al^{3+}$ can be well substituted into the $Ce^{4+}$ lattice site. The surface microstructures of the CSYA ceramics sintered at 1500 °C with various Al contents are shown in Fig. 3. The grain size of the pure sample (average 2 μm) is smaller than those of the other samples. When the Al contents were increased up to 0.5, the grain sizes and the densities of the samples gradually increased. After $x$ was 0.4, the average grain sizes were 5 μm. The grain densities of the CSYA ceramics at $x = 0.5$ were greater than those of the other samples. Fig. 4 shows the results of the AC impedance spectra analysis. The electrical properties of the CSYA ceramics were measured at 600 °C. Fig. 4 shows that the increase of Al content affected the bulk and grain boundary resistances of the CSYA ceramics. Normally, each arc of data points consists of bulk, grain boundary and electrode, respectively. Only one arc set can be seen for each sample because the bulk and grain boundary data are combined into one. It has been suggested that the resistance of a grain boundary is larger than the resistance of bulk. Another arc is the tail of the electrode. This phenomenon relies on the external environment of the samples and measuring state. When the Al content was increased up to 0.5, the data for the bulk and grain boundary gradually decreased to 0.4 and then increased. This occurred because the additional Al contents caused grain growth. The grain growth and grain boundary affected the sample's electrical properties [18–20]. The excess added Al produced lower grain boundary resistance. Fig. 3(e) shows the smallest grain size (5 μm). According to small grain size, the area of grain boundary and the ion conduction path became larger. Thus, when Al content is 0.4, grain boundary resistance is the smallest. This result indicates that the Al content affected the electrical resistance of the CSYA ceramics. Fig. 5 shows the Arrhenius plots of the total conductivity for the CSYA ceramics with various Al contents measured in the temperature range 500–700 °C. Ionic conductivity increased toward the high temperature area and when the Al content was increased, the value of ionic conductivity gradually increased, reaching its peak at 0.4. The maximum value of ionic conductivity measured at 600 °C is $7.1 \times 10^{-2}$ S cm$^{-1}$. This value is higher than reported in previous research of singly doped electrolytes such as $Ce_{1-x}Sm_xO_{2-y}$ (SDC) [21] and $Ce_{1-x}Y_xO_{2-y}$ (YDC) [22]. Moreover, it is higher than co-doped electrolytes such as $Ce_{0.8}Sm_{0.2-x}Y_xO_{1.9}$ [12]. This means that $Al^{3+}$ with its smaller ionic radius was substituted at the $Ce^{4+}$ site in the ceria lattice, and the increase in Al content resulted in the formation of oxygen vacancies. As a consequence, the increased Al content and oxygen vacancies enhanced ionic conductivity and electrical properties. Fig. 6 shows the activation energy of the CSYA ceramics, which was

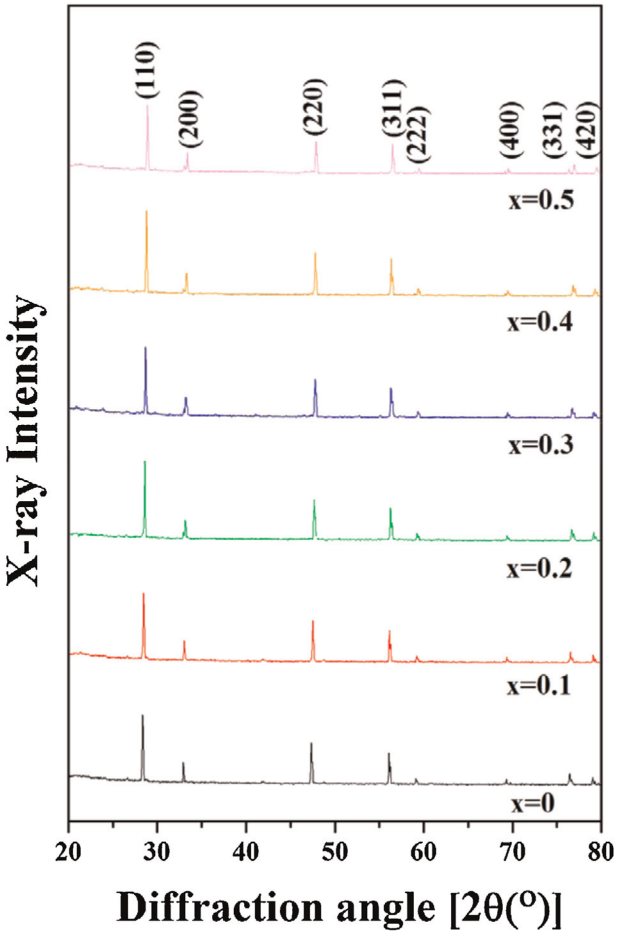

**Fig. 1.** X-ray diffraction patterns of $Ce_{0.8}(Sm_{0.5-x}Y_{0.5}Al_x)_{0.2}O_{2-\delta}$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5) ceramics.

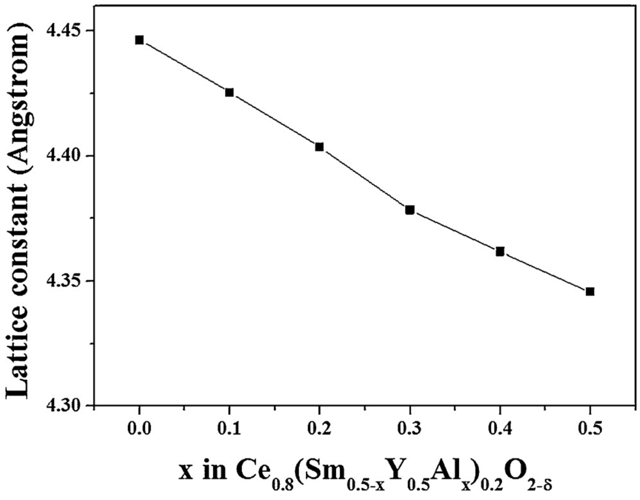

**Fig. 2.** Lattice constant as a function of various $Al_2O_3$ contents.