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Investigation of ionic conductivities of CeO_2-based electrolytes with controlled oxygen vacancies

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Abstract

Effects of Gd_2O_3 and SrO co-dopants on microstructural features, ionic conductivities and oxygen vacancy concentrations of two modified CeO_2 electrolytes ($Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ and $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$) are investigated using X-ray diffractometry (XRD), scanning electron microscopy (SEM) and AC impedance spectroscopy. Lattice parameters of co-doped CeO_2 specimens are observed to linearly increase with an increase of co-dopants amount, due to larger radius of Sr^{2+}. Grain size of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ is significantly larger than that of $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ at the same Sr^{2+} concentration, because $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ possesses more oxygen vacancy to migrate oxygen ions, defects and impurities easily, based upon calculation of oxygen vacancy amount. Small addition of SrO into 20 mol% Gd_2O_3 doped CeO_2 ($Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$) is effective in enhancing of ionic conductivity, but a sudden decreasing of conductivity with Sr^{2+} heavy-doping is found. The relationship among co-dopant concentration, oxygen vacancy radius, average binding energy and ionic conductivity in two different co-doped CeO_2 systems are discussed in this work.

Keywords: C. Ionic conductivity; D. CeO_2; C. Impedance; B. Grain size

1. Introduction

In conventional solid oxide fuel cells (SOFCs), the electrolyte material of choice is a high ionic conductor YSZ ($\sigma \sim 0.1$ S/cm, at 1000 °C). But the ionic conductivity of YSZ is small at low to intermediate temperatures. The high ionic conductivities of acceptor doped ceria at intermediate temperatures and reduction/oxidation behavior suggest them as promising candidates for electrochemical applications [1,2]. But oxygen ion migration is difficult in ceria because it induces the ionic conductivity of ceria to decrease with more than 20 mol% rare-earth cation. It is due to that the vacancies are not free and linked to dopant cations instead, a so-called 'defect association' between vacancies and cations is formed.

In addition to dopant concentration, ionic radius also affects the radius of oxygen vacancies and solid solution ratio of doping electrolyte [3]. If the ionic radius of the dopant is too large, then much strain is induced in the lattice of the electrolyte and the ionic conductivity decreases.

The co-doping method was reported as a novel principle to increase the ionic conductivity of ceria electrolyte in ceria-based systems [4,5]. But the reported ionic conductivity of $Ce_{0.94}Sm_{0.04}Y_{0.02}O_{1.97}$ specimen by Acres et al. is lower than that of GDC at 773 K [6]. It is found that the ionic conductivity performance of a co-doped system sometimes exhibits better and sometimes worse results. Hence, we would like to alloy the divalent and trivalent dopants of smaller ionic radii and lower lattice binding energies. Gd^{3+} and Sr^{2+} were chosen as dopants, because of their ionic radii close to the cerium cation and addition of Sr^{2+} to ceria increases the number of oxygen vacancies. Moreover, the average binding energy of GDC was reduced by adding strontium into GDC. In order to develop a new electrolyte for intermediate temperature solid oxide fuel cell, the conductivity mechanism was systematically studied in the co-doped ceria system and we expected that the ionic conductivity of GDC can be enhanced by doping appropriate amount of Sr^{2+} ion.

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2. Experimental

Electrolyte powder of Gd^{3+} and Sr^{2+} co-doped ceria $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ were prepared from Gd_2O_3 (99.9%, Nippon Yttrium Company Limited, Japan), $SrCO_3$ (99.5%, Cerac, USA) and CeO_2 (99.9%, Gredmann, China) using oxide-mixing method and calcining the resultant powders at 1300 °C for 5 h. The circular pellets of the co-doping system were formed by a cold pressing under a load of 2000 kg and sintered at 1500 °C for 15 h. The relative densities of these sintered specimens were higher than 98% of the theoretical density. Phase identification and solid solution conditions were analyzed using an X-ray diffractometer (M18XHF, MAC Science, Japan) with Cu-$K\alpha$ radiation. The microstructural features were inspected by scanning electron microscope (JEOL, JSM-6500) and the elemental segregation was measured by an energy dispersive spectrometer (EDS). The ionic conductivity of the specimens was determined by an ac impedance analyzer (Solartron 1260–1287). The impedance values were recorded in the frequency range of 0.1–1 MHz under specified temperatures between 300 °C and 800 °C in air. The activation energy for oxygen ion migration in a co-doped ceria specimen was calculated from the slope of the Arrhenius plot (ln σ versus $1/T$). The radius of oxygen vacancies for each specimen was computed using the ion packing model.

3. Results and discussion

Calculation of lattice parameters of the cubic phases in $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ systems provides more details on influences of SrO dopant as shown in Fig. 1. Lattice parameter of co-doped ceria specimens were observed to increase with an increase of Sr^{2+} content. In other words, the cell volume of the cubic phase increase with SrO content, the larger cell volume can be attributed to the larger ionic radius of Sr^{2+} (1.25 Å), compared to that of Gd^{3+} (1.05 Å) and Ce^{4+} (0.97 Å).

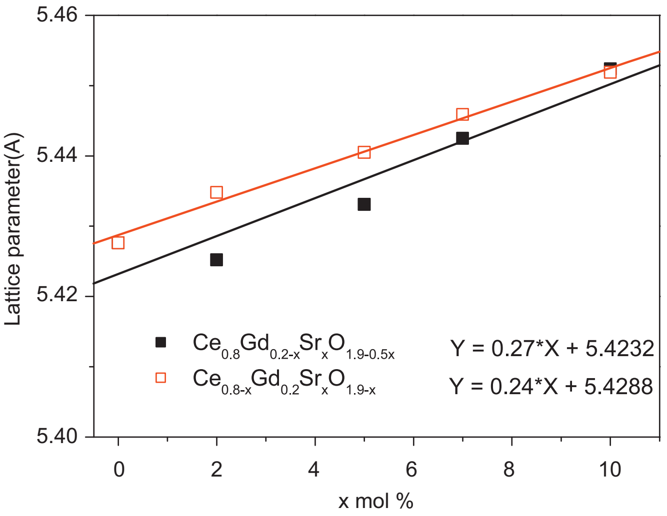

Fig. 1. Variation of lattice parameters in cubic-$Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and cubic-$Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens with different Sr^{2+} content.

Fig. 2 display the scanning electron micrographs of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens doped with various amounts of Sr^{2+} content. High dense specimens are found in two co-doped ceria system, and the average grain size of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ was found to increase from 3.5 μm to 16.5 μm with an increase of Sr^{2+} content as shown in Fig. 3. The observation indicates that the reason for the addition of SrO encourages the grain growth in SrO-doped GDC system, which reduces the amount of grain boundaries. No impurities were found to precipitate at the grain boundaries. The amount of co-dopants increases from 20 mol% to 30 mol% in $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ system. But, the average grain size of $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ system maintains at around a range of 10.5 μm to 12 μm, ascribed to that the amount of co-dopants in $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ system were fixed at 20 mol%. It reveals that there is a correlation between grain growth and the amount of co-dopants.

Fig. 4 shows the relationship between ionic conductivities and dopant contents in $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ systems of specimens at 800 °C. The ionic conductivity of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ specimen was observed to increase when x content increases to 2 mol%, but sudden decrease at x content is higher than 5 mol%. However, the ionic conductivities of $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens increase with an increase of dopant amount, and slightly decrease at high x values (>7 mol%). The variation of dopant amount and oxygen vacancy concentration in two different co-doped systems were calculated and listed in Fig. 4. It can be seen that ionic conductivity of two different co-doped ceria systems depends upon the amount of oxygen vacancy ($V_O^{\bullet\bullet}$). The best ionic conductivities of two co-doped ceria system were found in the range of $V_O^{\bullet\bullet}$ amount from 12 mol% to 15 mol% and a decrease of ionic conductivities while amount of $V_O^{\bullet\bullet}$ higher than 15 mol%. Comparison of the oxygen vacancy configuration in two co-doped ceria, different ionic conduction characteristics of the co-doped ceria systems were found by substituting Sr^{2+} into Ce^{4+} in the $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ system and by substituting Sr^{2+} into Gd^{3+} in the $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ system. Not only amount of oxygen vacancy, but also different valence of supplanted elements (as Ce^{4+} and Gd^{3+}) will affect the oxygen vacancy configuration and therefore induce different ionic conduction characteristics.

Fig. 5 shows the activation energy of co-doped ceria system seems to increase with a decrease of ionic conductivity, indicating that oxygen ion is not easy to move in the electrolyte matrix. Rapid increase of activation energy for total bulk conductivities of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ system was found while x higher than 2 mol%, it may be due to too much oxygen vacancy to form oxygen vacancy

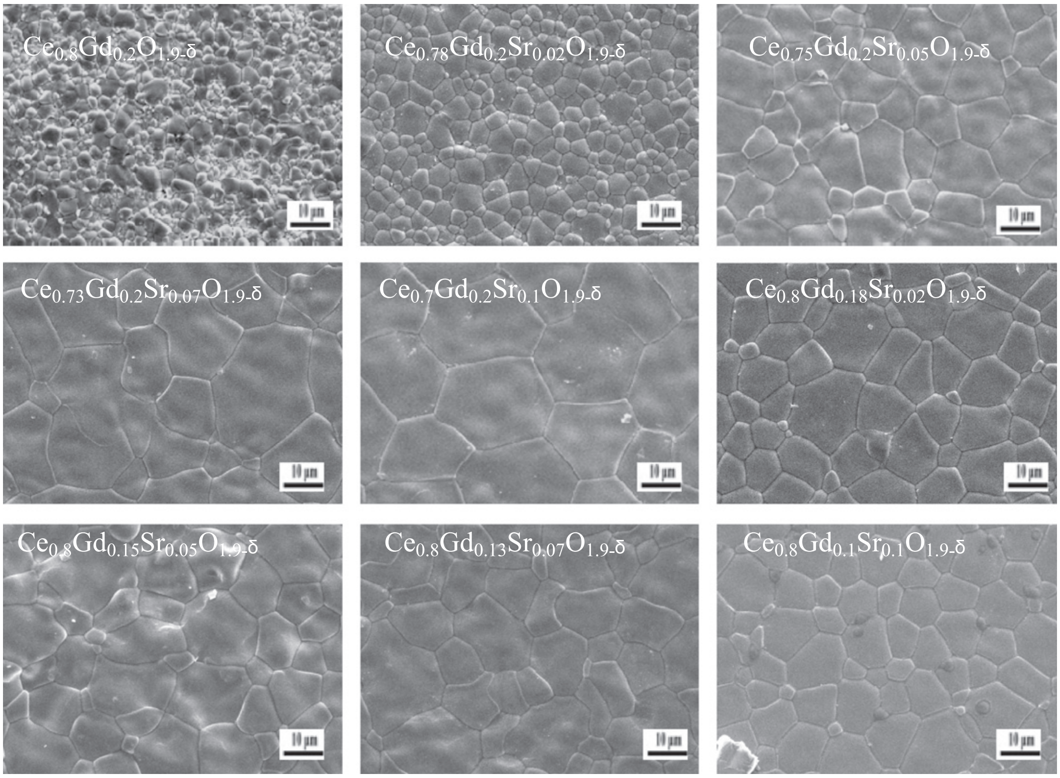

Fig. 2. Secondary electron images of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens with different Sr^{2+} content, wherein $x=0$, 0.02, 0.05, 0.07, 0.1.

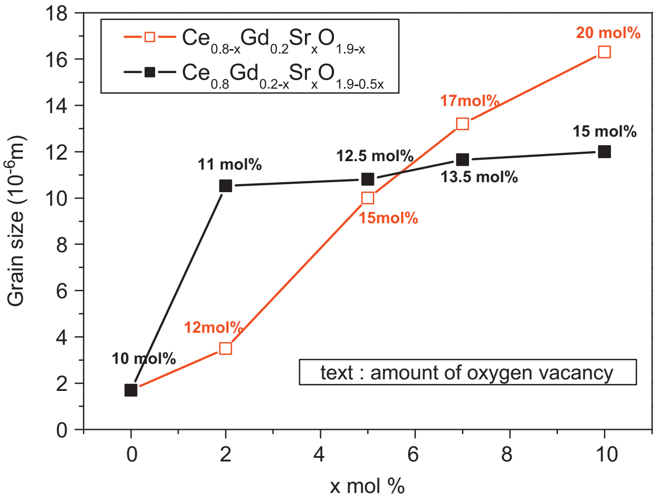

Fig. 3. Variation of grain size and oxygen vacancy amount in $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens with different Sr^{2+} content.

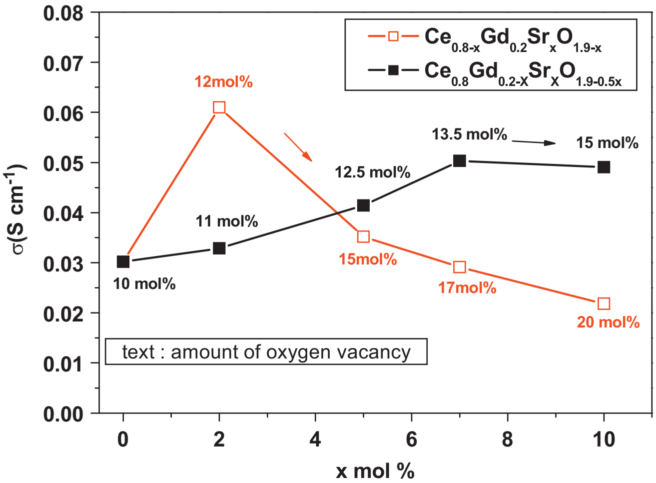

Fig. 4. Variation of ionic conductivity and oxygen vacancy amount in $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens with different Sr^{2+} content, wherein $x=0$, 0.02, 0.05, 0.07, 0.1.

clustering and therefore the bulk conductivity was reduced. There are no significant variation of activation energy for bulk conductivities in $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens, because the amount of oxygen vacancies are all less than the maximum amount of non-interference oxygen vacancies (fixed co-dopants amount at 20 mol%).

Average binding energies (ABE) [7] in the solid solutions of Gd^{3+} and Sr^{2+} co-doped ceria $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ can be expressed as Eq. (1):

$$\mathrm{ABE} = \frac{(0.8-x)}{8} \times \left[\mathrm{BE}_{CeO_2}\right] + \frac{0.2}{8} \times \left[\mathrm{BE}_{Gd_2O_3}\right] + \frac{x}{8} \times \left[\mathrm{BE}_{SrO}\right] \tag{1}$$

wherein BE is lattice binding energy for compounds, x is dopants concentration. The lattice binding energies

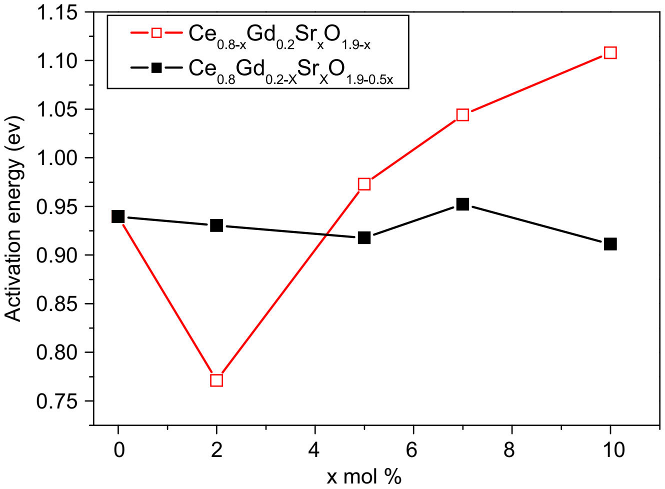

Fig. 5. Variation of activation energy for bulk conductivity of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens with different Sr^{2+} content, wherein $x=0$, 0.02, 0.05, 0.07, 0.1.

of CeO_2, SrO and Gd_2O_3 are 49.86 eV, 33.32 eV and 33.65 eV, respectively [7], it is reasonable to postulate that a decrease of average binding energy lowers the energy barrier for oxygen-ion diffusion and therefore the cation (M)–O bond length of Gd_2O_3 doped CeO_2 (GDC) matrix increases by SrO addition. After calculating the average binding energy, we concluded that addition of Sr^{2+} into GDC to decrease the value of average lattice binding energy of co-doped ceria system might be the reason why we observe an increase of ionic conductivity.

For comparison, the lattice parameters of Gd^{3+} and Sr^{2+} co-doped ceria system of specimens were calculated by an ion packing model [8]. The lattice parameter for an ideal fluorite structure can be calculated using the following Eq. (2):

$$a=\frac{4}{\sqrt{3}}(r_{\mathrm{anion}}+r_{\mathrm{cation}}) \tag{2}$$

where r_{anion} and r_{cation} are the radii of the dopant anions and cations, respectively. Since the actual lattice parameter of pure ceria is 5.414 Å from JCPDS cards, a multiplication factor of 5.414/5.473=0.9892 was taken in all of the above equations so that the lattice parameter of pure ceria becomes equal to 5.414 Å. Hence, the expression for the lattice parameter of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ can be written as shown in Eq. (3):

$$a=0.9892\times\frac{4}{\sqrt{3}}[(0.8-x)r_{\mathrm{Ce}}+0.2r_{\mathrm{Gd}}+xr_{\mathrm{Sr}}]+\frac{4}{\sqrt{3}}\left[(0.95-0.5x)r_{\mathrm{O}}+(0.05+0.5x)r_{V\ddot{O}}\right] \tag{3}$$

where $r_{V\ddot{O}}$ is the oxygen vacancy radii produced from co-doped cations in ceria. This equation was used for calculating the theoretical lattice parameters for Gd^{3+} and Sr^{2+} co-doped ceria solid solutions. In addition, the equation for the correlation between lattice parameter and co-dopants amount in $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ system of specimens can be written as Eq. (4):

$$a=0.9892\times\left[\frac{4}{\sqrt{3}}(r_{\mathrm{Sr}}-r_{\mathrm{Gd}})+\frac{1}{\sqrt{3}}\left(r_{V\ddot{O}}-r_{\mathrm{O}}\right)\right]x+\frac{4}{\sqrt{3}}(0.8r_{\mathrm{Ce}}+0.2r_{\mathrm{Gd}})+\frac{4}{\sqrt{3}}\left(0.95r_{\mathrm{O}}+0.05r_{V\ddot{O}}\right) \tag{4}$$

Average oxygen vacancy radii of co-doped $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ and $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ specimens were calculated to be 1.045 Å and 1.068 Å. It is confirmed that the radius of oxygen vacancies is dependent on the radii of single-/co-doped dopants. Oxygen ions migrate easily following an increase of oxygen vacancy radius and hence enhancement in the amount of open channel for oxygen vacancies. Larger radius of oxygen vacancy produces wider conducting channel in the structure, and therefore increases the conductivity of the specimens. Based upon the calculated results of oxygen radii in co-doped ceria system, oxygen vacancy radius of $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ system is larger than that of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ system. Thus, the ionic conductivities of the $Ce_{0.8}Gd_{0.2-x}Sr_xO_{1.9-0.5x}$ system are all higher than that of $Ce_{0.8-x}Gd_{0.2}Sr_xO_{1.9-x}$ system, especially the Sr^{2+} content at $x=0.02$. It indicates that the ionic conductivity of the co-doping ceria system was enhanced after modifying the maximum content of non-interfering oxygen vacancies and increasing oxygen vacancy radius in the material. The average radius of co-doping divalent cations is close to that of Ce^{4+} and average binding energy is as small as possible. Accordingly, the average radius of oxygen vacancies is a useful tool for estimating and qualitative analysis of the ionic conductivity of the co-doping system.

4. Conclusion

The origin of enhancement in ionic conductivity of a Gd^{3+} and Sr^{2+} co-doped ceria system was investigated. Systematic research on microstructural features and ionic conductivity of Gd^{3+} and Sr^{2+} co-doped ceria was carried out. The addition of Sr^{2+} content to GDC enhances the number of oxygen vacancies and decreases the association enthalpy and activation energy of GDC. In addition, decrease of average binding energy of co-doped ceria is another influential factor to enhance ionic conductivity due to addition of low lattice binding energy of SrO. The results demonstrate that ionic conductivity of co-doped ceria depends on the radii of oxygen vacancies. It seems that the ionic conductivity of the co-doping system can therefore be estimated based upon the ion packing model analysis. Accordingly, the ionic conductivity of the co-doping ceria system could be enhanced after modifying the maximum content of non-interfering oxygen vacancies and increasing oxygen vacancy radius in the material.

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