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Gd^{3+} and Sm^{3+} co-doped ceria based electrolytes for intermediate temperature solid oxide fuel cells

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Abstract

Co-doped ceria of $Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5a}$, wherein $a = 0.15$ or 0.2, $0 \leqslant y \leqslant a$, were prepared for intermediate temperature solid oxide fuel cells (ITSOFCs). Their structures and ionic conductivities were characterized by X-ray diffraction and AC impedance spectroscopy. All the electrolytes were found to be ceria based solid solutions of fluorite type structures. However, co-doping effect was observed more apparent for the electrolytes with $a = 0.15$ than for those with $a = 0.2$. In comparison to the singly doped ceria, the co-doped ceria of $Ce_{0.85}Gd_{0.15-y}Sm_yO_{1.925}$, wherein $0.05 \leqslant y \leqslant 0.1$, showed much higher ionic conductivities at 773–973 K. These co-doped ceria are more ideal electrolyte materials of ITSOFCs.

Keywords: Doped ceria electrolyte; Co-doping effect; Conductivity; Solid oxide fuel cells

1. Introduction

Doped ceria have been considered as one of the most promising electrolyte materials for intermediate temperature solid oxide fuel cells (ITSOFCs) [1,2]. These materials demonstrate much higher ionic conductivity at relatively lower temperatures in comparison to that of yttrium-stabilized zirconia (YSZ). Among the various dopants been studied, Gd^{3+} and Sm^{3+} singly doped ceria (abbreviated as CGO and CSO) were reported to have the highest conductivity [1,2]. Besides, many studies [3–5] have been carried out on co-doped ceria. However, controversial results on co-doping effect were reported. For example, Herle et al. [3] found that co-doped ceria with 3, 5, or 10 dopants showed significant higher ionic conductivity (by 10–30%) than the best singly doped materials, whereas, Yoshida et al. [5,6] found that a doubly doped ceria with La^{3+} and Y^{3+} did not show any synergistic effects on ionic conductivity. Since CGO and CSO are believed the most conductive electrolytes [1,2], Gd^{3+} and Sm^{3+} co-doped ceria are probably good and even better electrolytes. However, there is still a lack of study reported on these materials. In this work, Gd^{3+} and Sm^{3+} co-doped ceria materials were prepared and characterized. The effect of co-doping on structure and conductivity was studied in comparison to singly doped ceria. High conductive electrolytes were found.

2. Experimental

The starting materials were the nitrate salts of reagent grade (Acros) and used as purchased. The aqueous solutions of each metal ion of Ce^{3+}, Gd^{3+}, and Sm^{3+} were prepared by dissolving the nitrate salt in distilled water and diluting them to desired concentrations. An aqueous solution of citric acid (CA) and polyethylene glycol (PEG) in a weight ratio of CA/PEG = 60 was also prepared and was termed as CP solution. According to the composition ($Ce_{1-a}Gd_{a-y}Sm_yO_{2-y}$, wherein $a = 0.15$ or 0.2, $0 \leqslant y \leqslant a$) of the electrolyte samples, different

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volumes of metal ion solutions were taken and mixed in a beaker. Then, CP solution was added until the molar number of citric acid was equal to the total number of the metal ions in the beaker. The mixed solution was evaporated under stirring at 353 K until the solution gelled. The gel was dried at 378 K, ground and calcined in air at 973 K for 4 h, and then ground again to form calcined powder. The powder was uniaxially pressed under 750 MPa into green pellets using a stainless steel die with 13 mm diameter. The green pellets were further sintered at 1773 K for 14 h to form dense pellets.

For structure analysis, the dense pellets were ground to powder again and were identified at room temperature using a PANalytial X-ray diffractometer (XRD) (Cu Kα radiation, 45 kV, 40 mA). For conductivity measurement, Ag paste was brushed onto both sides of the dense pellet, and then sintered at 1073 K for 30 min to form Ag electrodes. Pt leads were attached to the electrodes using Ag paste and were sintered again at 1073 K for 30 min. Impedance was measured using the two probe method with a Autolab Impedance Analyzer over the frequency range of 0.01 Hz–1 MHz and with a voltage amplitude of 30 mV. The measurements were taken at constant temperatures within 473–973 K and in air (25 sccm).

3. Results and discussion

3.1. Crystal structures

For all the ceria based electrolyte samples of this work, it was found that the doped ceria pellet samples (sintered at 1773 K) showed the same XRD patterns as the powder samples (just calcined at 973 K) of the same compositions, except that the XRD peaks were much sharper for the former than for the latter, and that the XRD patterns of the doped ceria samples are different from those of pure Gd_2O_3 and Sm_2O_3, but similar to that of pure CeO_2. These results indicate that the doped ceria samples are all solid solutions of fluorite type structures that were formed in the calcining process and crystallized better in the sintering process.

More accurate XRD measurement with quartz as inner standard showed that the 2θ values of the doped ceria shift slightly toward lower angle in comparison to that of pure CeO_2. This is because the ionic radius decreases in the order of $Sm^{3+}>Gd^{3+}>Ce^{4+}$, the substitution of Ce^{4+} with Sm^{3+} and Gd^{3+} in the lattice of CeO_2 would enlarge the crystal lattice. As shown in Fig. 1, the lattice constant of $Ce_{1-y}Gd_yO_{2-0.5x}$ and $Ce_{1-y}Sm_yO_{2-0.5y}$ increased linearly with y, but the slope is lower for the former (0.0813) than for the latter (0.134) because Gd^{3+} is smaller than Sm^{3+}. For the same reason, the lattice constant of $Ce_{0.85}Gd_{0.15-y}Sm_yO_{1.925}$ and $Ce_{0.8}Gd_{0.2-y}Sm_yO_{1.9}$ both increased linearly with y, and for the same y, the lattice constant was smaller for $Ce_{0.85}Gd_{0.15-y}Sm_yO_{1.925}$ than for $Ce_{0.8}Gd_{0.2-y}Sm_yO_{1.9}$. The results in Fig. 2 follows Vegard's rule [7], further suggesting that all the doped ceria samples of this work are ceria based solid solutions.

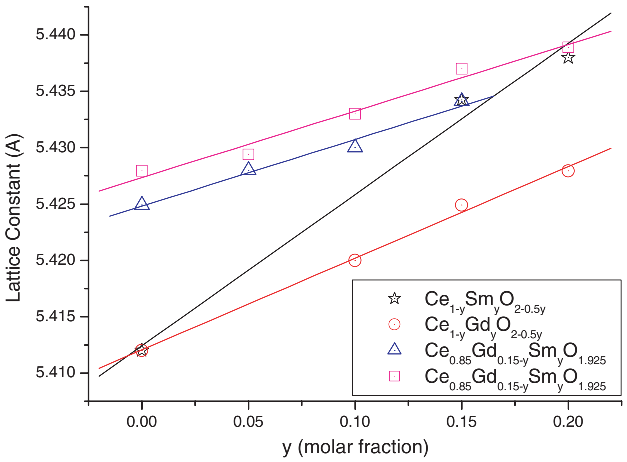

Fig. 1. Dependence of lattice constant on the composition (y) of different doped ceria electrolytes (sintered at 1773 K for 14 h).

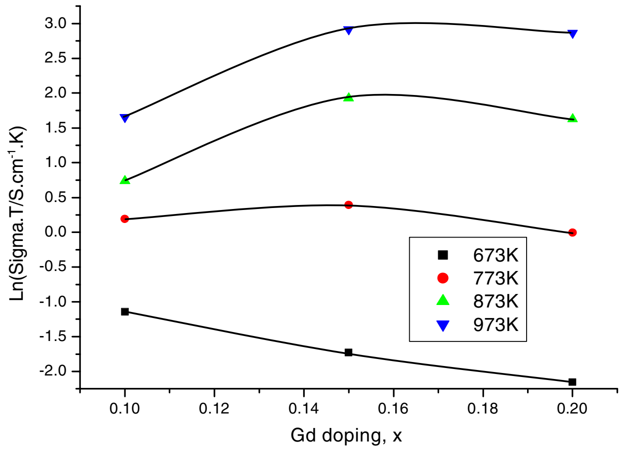

Fig. 2. Effect of Gd doping (x) on the conductivity of pellet samples with nominal composition of $Ce_{1-x}Gd_xO_{2-0.5x}$ in air and at different temperatures.

3.2. Conductivities

It was documented that the main contribution of the conductivity of ceria based compounds in air was oxide ionic conductivity (>99.5%) and that from electronic conductivity was negligible [2,8]. In this paper, the conductivity measured in air was treated as the oxide ionic conductivity only. In the following context, the word "*conductivity*" is used to represent the total conductivity of grain and grain boundary.

Fig. 2. shows the conductivities of $Ce_{1-x}Gd_xO_{2-0.5x}$, wherein $0.1 \leqslant x \leqslant 0.2$ in air and at 473–973 K in the form

of ln(σ T) vs. x. It can be seen that the maximum conductivity emerged at $x = 0.15$ when temperature $\geqslant 773$ K, but at $x = 0.1$ when temperature <773 K. At 773–973 K, the operating temperature of ITSOFC, the samples with $x = 0.15$ and 0.2 showed higher conductivity than that with $x = 0.1$. Therefore, in the following co-doping effect study, total dopant content was confined to 0.15 and 0.2.

In order to investigate co-doping effect and at the same time avoid the effect of oxide ion vacancy concentration, a set of samples with nominal composition of $Ce_{0.85}Gd_{0.15-y}Sm_yO_{1.925}$, wherein $0 \leqslant y \leqslant 0.15$, were prepared and studied. The conductivities of these samples in air and at different temperatures were shown in Fig. 3 in the form of ln(σ T) vs. y. It can be seen that co-doped samples showed apparently higher conductivities than singly doped samples. This suggests that co-doping effect exists. At 973 K, the conductivity of the co-doped samples reached the maximum of 0.0475 S cm^{-1}, higher than the best results in the literatures for CGO (0.0316 S cm^{-1}) [9] and CSO (0.041 S cm^{-1}) [10].

Similarly, another set of samples with nominal composition of $Ce_{0.8}Gd_{0.2-y}Sm_yO_{1.9}$, wherein $0 \leqslant y \leqslant 0.2$, were prepared and studied. The conductivities of these samples in air and at different temperatures were shown in Fig. 4 in the form of ln(σ T) vs. y. It can be seen that the conductivities of the co-doped ceria were higher than those of the singly doped ceria when temperature $\leqslant 773$ K, but between those of the singly doped ceria when temperature >773 K. This suggests that co-doping effect exists here only when temperature $\leqslant 773$ K. Similarly, the changes of co-doping effect in different temperature ranges were also observed on $Ce_{0.9}Sm_{0.03}Y_{0.03}O_x$, and ceria doped with La^{3+} and Y^{3+} [3–6].

Co-doping effect has been discussed in terms of configurational entropy [11]. Comparing with singly doped ceria solid solution, co-doped ceria solid solution had larger configurational entropy, and therefore had higher ionic conductivity. However, this theory can not explain the fact that $Ce_{0.85}Gd_{0.1}Sm_{0.05}O_{1.925}$ and $Ce_{0.85}Gd_{0.05}Sm_{0.1}O_{1.925}$ has similar configurational entropy, but the former showed higher conductivity then the latter (see Fig. 3), and that $Ce_{0.8}Gd_{0.15}Sm_{0.05}O_{1.9}$ had higher configurational entropy than $Ce_{0.85}Gd_{0.1}Sm_{0.05}O_{1.925}$, but the former showed lower conductivity than the latter (see Figs. 3 and 4). It has been proved that the ionic conductivity of doped ceria is related to the lattice distortion [1,2]. Therefore, the co-doping effect must be related not only to configurational entropy but also to the lattice distortion away from pure CeO_2. Because $Ce_{0.85}Gd_{0.1}Sm_{0.05}O_{1.925}$ has a lattice constant more close to pure CeO_2 than $Ce_{0.85}Gd_{0.05}Sm_{0.1}O_{1.925}$ (as shown in Fig. 1), the former has higher ionic conductivity than the latter. For the same reason, $Ce_{0.85}Gd_{0.1}Sm_{0.05}O_{1.925}$ has higher ionic conductivity than $Ce_{0.8}Gd_{0.15}Sm_{0.05}O_{1.9}$.

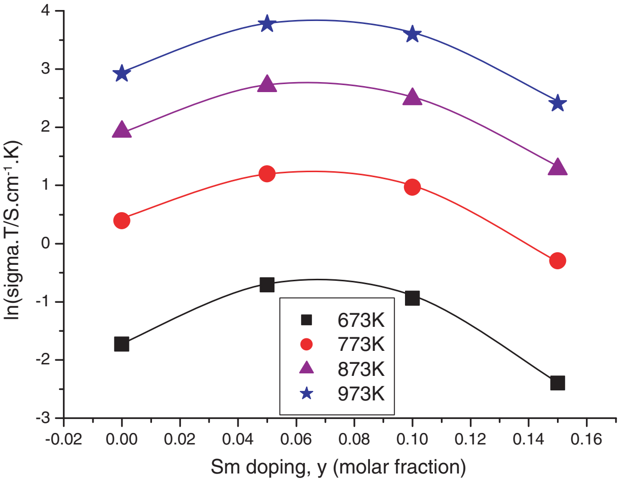

Fig. 3. Effect of Sm doping (y) on the conductivity of pellet samples with nominal composition of $Ce_{0.85}Gd_{0.15-y}Sm_yO_{1.925}$ in air and at different temperatures.

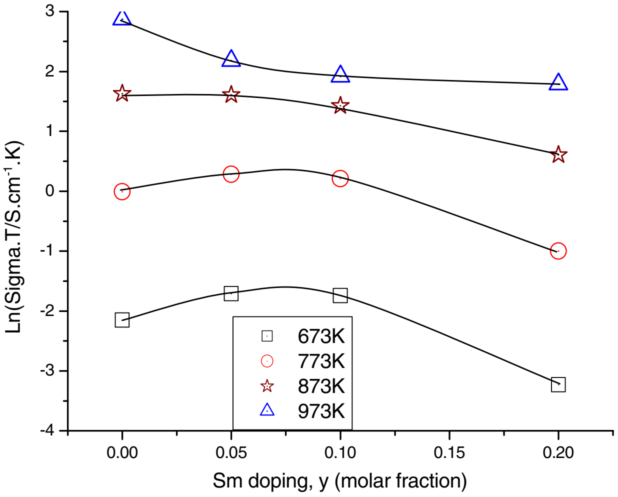

Fig. 4. Effect of Sm doping (y) on the conductivity of pellet samples with nominal composition of $Ce_{0.8}Gd_{0.2-y}Sm_yO_{1.9}$ in air and at different temperatures.

4. Conclusions

Co-doped ceria with nominal composition of $Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5a}$, wherein $a = 0.15$ or 0.2, $0 \leqslant y \leqslant a$, were prepared and studied in comparison to singly doped ceria on the structure and conductivity. The crystal structures of all the samples were fluorite type ceria based solid solutions. Co-doping effect was observed more apparent for the samples with $a = 0.15$ than for those with $a = 0.2$. In comparison to the singly-doped ceria, the co-doped ceria of $Ce_{0.85}Gd_{0.15-y}Sm_yO_{1.925}$, wherein $0.05 \leqslant y \leqslant 0.1$, showed much higher ionic conductivities at 773–973 K. These co-doped ceria are more ideal electrolyte materials of ITSOFCs.

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