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Effect of Sm and Mg co-doping on the properties of ceria-based electrolyte materials for IT-SOFCs

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ABSTRACT

Samples of Sm and Mg co-doped ceria electrolytes of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ ($x = 0$, 0.05, 0.10, 0.15 and 0.20) were sintered from powders obtained by solid-state reaction method. The structures and electrical properties were characterized by X-ray diffraction (XRD) and AC impedance spectroscopy (IS). The thermal expansion curves of samples were measured and the thermal expansion coefficients between 100 and 800 °C were calculated. Results showed that co-doping with appropriate ratio of Sm and Mg can improve the electrical performance of ceria-based electrolytes. As the substitution amount of Mg for Sm increased up to 50 mol%, the conductivity of the samples maintained almost unchanged or even slightly higher than that doped only with Sm in intermediate temperature. The results suggest that the materials cost for producing the ceria-based intermediate temperature solid oxide fuel cells (IT-SOFCs) may be significantly reduced owing to the cost difference between Mg and Sm.

1. Introduction

Solid oxide fuel cells (SOFCs) have been attracting a great attention as a promising technique for electrical power generation due to its higher efficiency, high waste-heat utilization, environmental friendship, and greater fuel flexibility [1]. A conventional SOFC using 8 mol% yttria-stabilized zirconia (YSZ) as electrolyte requires operating at high temperature of 800–1000 °C. But this necessity of high-operating temperature has resulted in high cost, physical and chemical degradation of component materials. Therefore, it becomes increasingly important to reduce the operating temperature of the SOFC, and the development of intermediate temperature (600–800 °C) SOFCs (IT-SOFCs) is the key to commercialization. Doped ceria has been considered as one of the most promising electrolyte materials for IT-SOFCs because of high oxide ionic conductivity and good compatibility with electrodes [2–4].

The ionic conductivity of ceria resulting from oxygen vacancies depends on the dopants and their amount [5,6]. It increases significantly when ceria is doped with aliovalent oxides such as Y_2O_3 and various rare earth oxides. However, an increasing amount of dopants tends to form a second phase due to the solubility limit, resulting in the reducing of the conductivity. Generally, the critical dopant concentration to achieve the optimum conductivity is approximately 20 mol% [7]. Some doped electrolytes, such as $Ce_{1-x}Gd_xO_{2-y}$ (GDC), $Ce_{1-x}Sm_xO_{2-y}$ (SDC) and $Ce_{1-x}Y_xO_{2-y}$ (YDC), show relatively high oxide ionic conductivity. In order to further increase conductivity and improve other related properties of the materials, co-doping approach have been extensively conducted and proved to be effective. Herle et al. [8] found that co-doping ceria with alkaline earth and rare earth ion showed significantly higher conductivity in air than the best singly doped materials with the same oxygen concentration. $Ce_{0.8}Sm_{0.2-x}Y_xO_{1.9}$ [9], $Ce_{0.85}Gd_{0.1}Mg_{0.05}O_{1.9}$ [10], $Ce_{1-x-y}Sm_xCa_yO_{2-z}$ [11], $Ce_{1-a}Gd_{a-y}Sm_yO_{2-0.5a}$ [12], and $Ce_{1-x-y}Gd_xPr_yO_{2-z}$ [13] are well-known examples.

On the other hand, how to reduce the cost of the materials is also of interesting for the application of these electrolytes. Sm_2O_3 singly doped ceria were reported to have the highest conductivity among the singly doped ceria [14,15], but the cost of Sm_2O_3 is relatively much high. Therefore, it is important to develop cost-effective ceria-based electrolyte materials with desired ionic conductivity for IT-SOFCs.

Considering the low cost and high stability of MgO and possible co-doping effect, Sm and Mg co-doped ceria was prepared and characterized in this research. The effect of the addition of Mg to Sm doped ceria on its properties was investigated. Special attention is paid to the optimum addition amount of Mg, aiming maximum substitution of Mg to Sm not at the expense of lowering the performance.

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2. Experimental

A series of solid solution with the general formula of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ ($x = 0$, 0.05, 0.10, 0.15 and 0.20) were synthesized by solid-state reaction method using CeO_2 (99.5%), Sm_2O_3 (99.5%), and MgO (99.0%) as starting materials. The raw materials were weighted according to stoichiometric ratio and thoroughly mixed with distilled water for 8 h, using zirconia (ZrO_2) milling media in a planetary mill. After dried, the powders were ground and then calcined at 1200 °C in air for 2 h. The as-synthesized powders were milled again with distilled water for 6 h and dried. For conductivity measurement, the dried powders were ground with 5 wt.% PVA solution in an agate mortar and then die-pressed into cylindrical pellets (13 mm in diameter and 1 mm in thickness) under a pressure of about 150 MPa. The green pellets were then sintered at 1550 °C in air for 2 h. Bars of 62 mm × 5 mm × 5 mm mm were also pressed at 100 MPa for thermal expansion test. Densities of the sintered pellets were determined by Archimedean method.

The crystal structure of the pellets (ground to powder again for measurement) was identified at room temperature via X-ray diffraction (XRD, D/max-III, Rigaku) with Cu Kα radiation in the 2θ range from 20° to 80°. Thermal expansion measurements were conducted with a dilatometer (RPZ-01, Luoyang, China), operated from room temperature to 800 °C in air (heating rate 5 °C/min). The cross-section micrographs of sintered samples were observed using scanning electron microscopy (SEM, Model JSM-5900, JEP, Tokyo, Japan).

The oxide ionic conductivity of the materials was measured by electrochemical impedance spectroscopy based on the sintered pellets. Both sides of the pellets were coated with silver paste and then heated at 600 °C for 30 min before the measurement to ensure good bonding. The AC impedance spectra of the pellets were measured using an impedance analyzer (PARSTAT 2273). The measurements were conducted in air in the temperature range from 500 to 750 °C and in the frequency range from 0.1 Hz to 1 MHz with an increment of 50 °C. Curve fitting and resistance calculation were done by ZSimpWin software, using the expression of $\sigma = L/SR$, where L is the sample thickness and S is the electrode area of the sample surface.

3. Results and discussion

3.1. Phase composition

The XRD patterns of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ samples sintered at 1550 °C are shown in Fig. 1. It can be seen that only a cubic CeO_2 ($Fm3m$) phase was identified and the 2θ values of the doped ceria shift slightly towards higher angels with x changes from 0 to 0.20. Cell parameters were calculated by fitting the observed XRD reflections of five samples sintered at 1550 °C. Fig. 2 shows the relationship between unit cell parameters and dopant concentration. As can be seen, the cell parameters decrease with x (magnesium concentration) increasing in the investigated substitution range of $x = 0$–0.20. According to the elastic energy, Kim's expression implies that the critical radius (effective ionic radius) of ceria doping with divalent and trivalent metals is 0.1106 and 0.1038 nm, respectively [6]. The radius of Sm^{3+} (0.1219 nm) is larger than the critical radius and radius of Mg^{2+} (0.103 nm) is smaller than the critical radius, therefore, the cell parameter decreases with increasing Mg^{2+} concentration, which indicates that Sm and Mg are well into the crystal lattice of ceria.

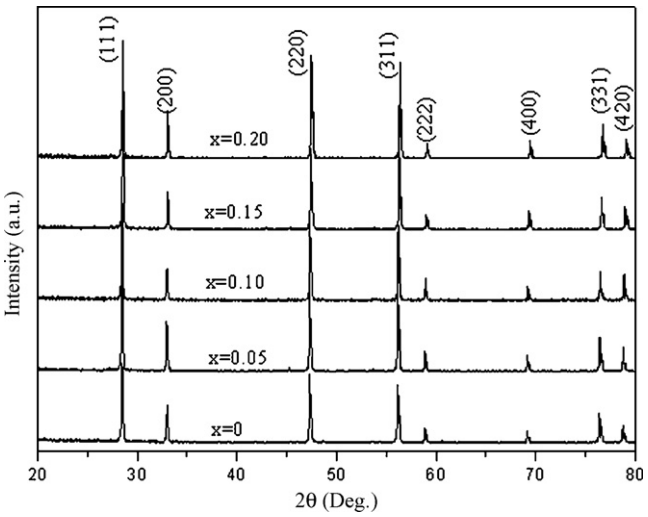

Fig. 1. XRD patterns of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ sintered at 1550 °C.

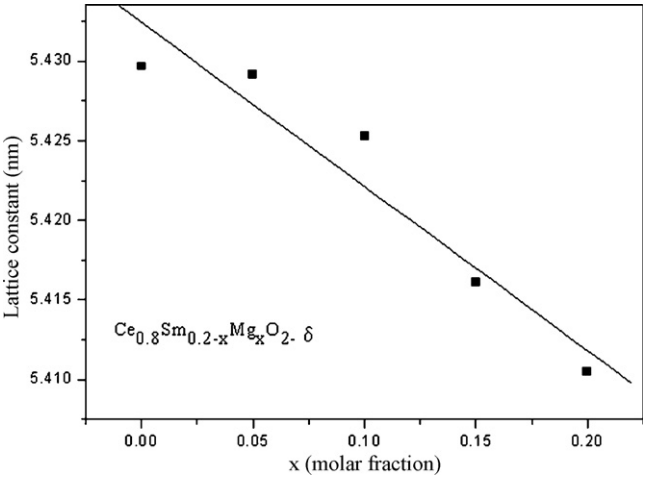

Fig. 2. Relationship of unit cell parameters and dopant concentration of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$.

3.2. TEC measurements

Fig. 3 shows the thermal expansion curves of $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ samples, all the samples showed linear

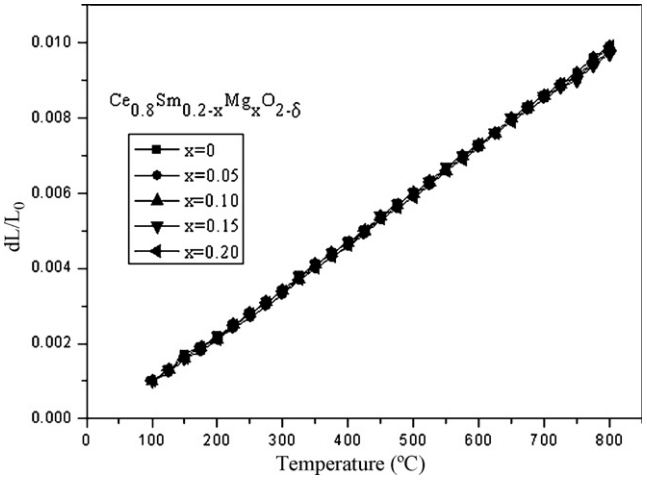

Fig. 3. Linear thermal expansion curves for $Ce_{0.8}Sm_{0.2-x}Mg_xO_{2-\delta}$ in air.