Special Issue of the 7th International Advances in Applied Physics and Materials Science (APMAS 2017)

Ionic Conductivity of $Ce_{0.9-x}Gd_{0.1}Sm_xO_{2-\delta}$ co-doped Ceria Electrolytes

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Ceria doped with heterovalent cations, such as alkaline earth and rare earth ions, has been considered one of the most promising electrolyte materials for intermediate temperature solid oxide fuel cells. The present trend is to investigate the co-doping approach in ceria to improve further its electrical conductivity. In this study, $Ce(NO_3)_3{\cdot}6H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$ nitrate salts were used as the starting materials to form co-doped ceria electrolytes of $Ce_{0.9-x}Gd_{0.1}Sm_xO_{2-\delta}$ ($x = 0$, 0.05, 0.10) using the Pechini method. The samples were characterized by means of X-ray diffraction, scanning electron microscopy and electrochemical impedance spectroscopy methods. The results of the impedance spectroscopy revealed that $Ce_{0.85}Gd_{0.10}Sm_{0.05}O_{1.925}$ sample exhibited the highest ionic conductivity of 4.23×10^{-2} Scm^{-1} at 750 °C in air.

DOI: 10.12693/APhysPolA.134.122

PACS/topics: co-doped ceria, Pechini method, samarium, gadolonium, solid oxide fuel cell

1. Introduction

Solid oxide fuel cell (SOFC) is a promising kind of energy conversion device [1]. SOFC consists of three parts, anode, cathode and electrolyte. The electrolyte plays a very important role, i.e. it acts as a barrier between the electrodes and helps in transferring the O^{2-} ions between the electrodes [2–4]. In conventional SOFC, yttria-stabilized zirconia (YSZ) is used as the electrolyte material, which requires high temperature (1000 °C) for the cell operation. However, such high temperature causes thermal degradation, thermal expansion mismatch and even the interfacial reaction between electrodes and electrolyte [5, 6]. Therefore, it is essential to develop new cost-effective electrolytes with high ionic conductivity at intermediate temperatures (≤ 800 °C).

Co-doped ceria-based electrolytes have attracted much interest in recent years. Among these new electrolyte materials, ceria doped with heterovalent cations such as rare earth and alkaline earth metal ions have been widely investigated as the solid electrolytes for intermediate temperature solid oxide fuel cells [7, 8]. As reported [9], the single element doped electrolytes, such as $Ce_{1-x}Sm_xO_{2-y}$ and $Ce_{1-x}Gd_xO_{2-y}$ etc., display high oxide ion conductivity.

Considering the high ionic conductivity at intermediate temperature and high stability of rare earth doped CeO_2, the Gd and Sm co-doped ceria was prepared and characterised in this study. The effect of Gd/Sm co-doping on the performance of ceria electrolyte was investigated systematically. Our aim is to develop better new ceria-based electrolyte materials for intermediate-temperature solid oxide fuel cells.

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2. Experimental

2.1. Synthesis

$Ce(NO_3)_3{\cdot}6H_2O$, $Gd(NO_3)_3{\cdot}6H_2O$, $Sm(NO_3)_3{\cdot}6H_2O$ nitrate salts were used as metal precursors and ethylene glycol (R.P.Normopur), citric acid (Boehringer Ingelheim) were selected for the polymerization treatment. $Ce_{0.9-x}Gd_{0.1}Sm_xO_{2-\delta}$ electrolytes were synthesized by the Pechini method. More details about the Pechini method are reported in our earlier work [10].

2.1. Characterization

XRD technique was used to determine the crystal structure and phase purity of samples. The X-ray spectra of the Sm and Gd co-doped ceria particles were obtained over the 2θ range of 10°–90° by using Rigaku D/max-2200 PC X-ray difractometer with Cu-K_α radiation.

The calcined powders were pressed into disks at 200 MPa using cold isostatic pressing. The compact disk of $Ce_{0.9-x}Gd_{0.1}Sm_xO_{2-\delta}$ powders was then sintered at 1400 °C for 6 hours after heating with a heating rate of 5 °C/min. The densities of the sintered discs D_{pellet} were determined by using the well-known Archimedes method [10]. The microstructure of the sintered pellets was characterized by means of SEM using FEI Quanta FEG 450 microscope.

The ionic conductivity measurements of the sintered pellets were carried out using an AC impedance analyzer (Solartron 1260 FRA and 1296 interface) in the temperature range of 300–800 °C in air. Curve fitting and resistance calculations were carried out using Zview software, using equation $\sigma = L/SR$, where L and S represent sample thickness and electrode area of the sample, respectively. The activation energies E were calculated by fitting the conductivity data to the Arrhenius relation for thermally activated conduction, expressed in Eq. (1):

$$\sigma = \frac{\sigma_0}{T}\exp\left(-\frac{E_a}{kT}\right), \quad (1)$$

where T is temperature in K, σ is total conductivity at temperature T, σ_0 is a pre-exponential factor, $E_a = \Delta H_m + \Delta H_a$ is the activation energy, and k is Boltzmann constant. ΔH_m and ΔH_a denote the migration enthalpy and association enthalpy of the oxygen vacancy, respectively. σ_0 is related to the oxygen vacancy concentration and vibrational frequency of the lattice.

3. Results and discussion

3.1. Phase analysis

Figure 1a shows that when $x = 0 - 0.10$, the samples are single phase with a cubic fluorite structure similar to CeO_2, without additional peaks, which confirms the complete dissolution of the dopants into the host CeO_2 lattice. (JCPDS powder diffraction File No. 34-0394). Introduction of Gd^{3+} and Sm^{3+} into Ce^{4+} can cause a small shift in the ceria peaks.

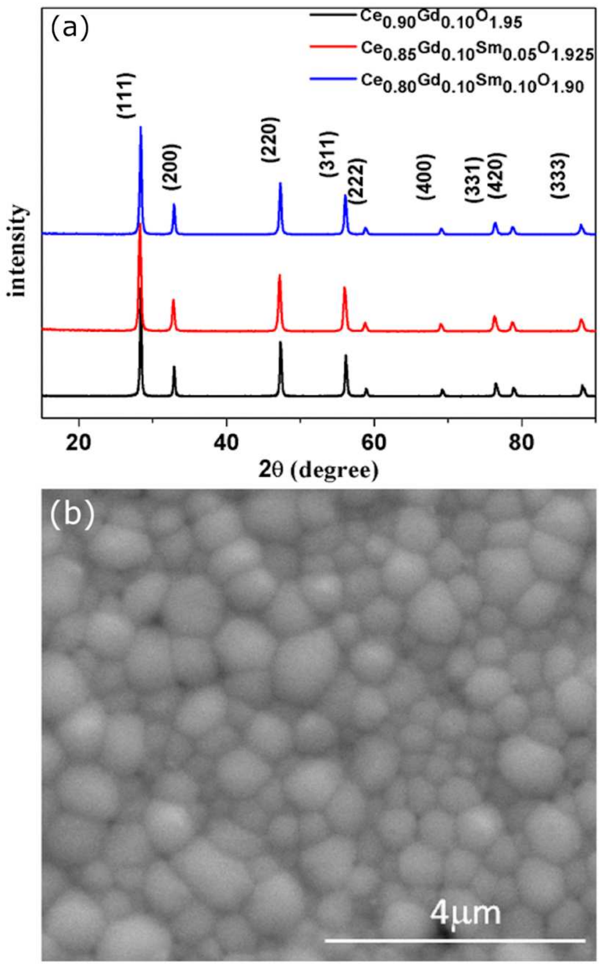

Fig. 1. (a) XRD patterns of $Ce_{0.9-x}Gd_{0.1}Sm_xO_{2-\delta}$ (x = 0, 0.05, 0.10) calcined at 600 °C for 4 h, (b) the SEM picture of $Ce_{0.85}Gd_{0.10}Sm_{0.05}O_{1.925}$.

3.2. Microstructure

Figure 1b shows the SEM image of the $Ce_{0.85}Gd_{0.10}Sm_{0.05}O_{1.925}$ sample sintered at 1400 °C for 6 h. It is clearly seen that the surface of the sample is highly dense. This situation is in good agreement with the relative density of the sample which is over 94%. The compactness of the sample has probably increased the conductivity.

3.3. Ionic conductivity

Figure 2 shows the impedance spectra of $Ce_{0.9}Gd_{0.10}Sm_xO_{2-d}$ sample measured under air atmosphere at 750 °C. It shows that $Ce_{0.85}Gd_{0.10}Sm_{0.05}O_{1.925}$ electrolyte has a relatively small total resistance compared to those of $Ce_{0.9-x}Gd_{0.1}Sm_xO_{2-\delta}$ (x = 0, 0.10). Therefore, $Ce_{0.85}Gd_{0.10}Sm_{0.05}O_{1.925}$ is expected to exhibit good electrical conductivity. The total conductivity of the $Ce_{0.85}Gd_{0.10}Sm_{0.05}O_{1.925}$ was about 4.8 times that of singly Gd-doped ceria at 750 °C.

In this study, for $Ce_{0.9-x}Gd_{0.1}Sm_xO_{2-\delta}$ samples, the partial substitution of Ce with Sm is thought to change the concentration of the oxygen vacancy. This is probably due to the oxygen vacancies that are introduced in CeO_2 by doping with low-valency metal oxides. Thus, the Kröger-Vink notation, as given in Eqs. (2) and (3) can be expressed as follows [5, 9]:

$$Sm_2O_3 \xrightarrow{CeO_2} 2Sm'_{Ce} + 3O_0^x + V_0^{00}, \quad (2)$$

$$Gd_2O_3 \xrightarrow{CeO_2} 2Gd'_{Ce} + 3O_0^x + V_0^{00}. \quad (3)$$

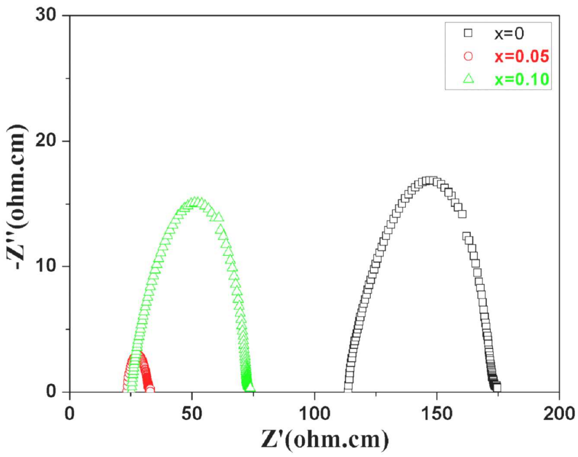

Fig. 2. AC impedance of the $Ce_{0.9-x}Gd_{0.1}Sm_xO_{2-\delta}$ system at 750 °C.

The addition of Gd_2O_3 and Sm_2O_3 into the CeO_2 system would lead to the formation of more oxygen vacancies because of the charge compensation in electrolyte materials.

4. Conclusions

All synthesized Gd and Sm co-doped samples calcined at 600 °C were fluorite-type ceria-based solid solutions obtained in the sintering process at 1400 °C. The results of the ionic conductivity measurements of Gd and Sm co-doped ceria indicate that an appropriate Gd to Sm ratio increases the ionic conductivity compared to those in singly Gd doped cases. The total conductivity increases owing to the change in oxygen vacancy concentration. The optimal doping ratio of Sm in the co-doped system was $x = 0.05$.

Acknowledgments

This research work was supported by the Scientific and Technological Research Council of Turkey (TÜBITAK), Grant No: MAG-114M238, Research Fund of the Istanbul University, project No. 24959 and 23196.

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