Ionic Conductivity of Ce$_{0.9-x}$Gd$_{0.1}$Sm$_x$O$_{2-\delta}$ 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$_3$)$_2$·6H$_2$O, Gd(NO$_3$)$_3$·6H$_2$O, Sm(NO$_3$)$_3$·6H$_2$O nitrate salts were used as the starting materials to form co-doped ceria electrolytes of Ce$_{0.9-x}$Gd$_{0.1}$Sm$_x$O$_{2-\delta}$ ($x = 0, 0.05, 0.10$) 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 $4.23 \times 10^{-2}$ Scm$^{-1}$ at 750$^\circ$C in air.

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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$^\circ$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 ($\leq$ 800$^\circ$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$_x$O$_{2-\gamma}$ and Ce$_{1-x}$Gd$_x$O$_{2-\gamma}$ 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.

2. Experimental

2.1. Synthesis

Ce(NO$_3$)$_3$·6H$_2$O, Gd(NO$_3$)$_3$·6H$_2$O, Sm(NO$_3$)$_3$·6H$_2$O nitrate salts were used as metal precursors and ethylene glycol (R.P.Normapur), citric acid (Boehringer Ingelheim) were selected for the polymerization treatment. Ce$_{0.9-x}$Gd$_{0.1}$Sm$_x$O$_{2-\delta}$ 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$^\circ$–90$^\circ$ by using Rigaku D/max-2200 PC X-ray diffractometer with Cu-K$_{\alpha}$ 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$_x$O$_{2-\delta}$ powders was then sintered at 1400$^\circ$C for 6 hours after heating with a heating rate of 5$^\circ$C/min. The densities of the sintered discs $D_{\text{pellet}}$ 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$^\circ$C in air. Curve fitting and resistance calculations were carried out using Zview software, using equation $\sigma = L/S\,R$, 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):

\begin{equation}
\sigma = \sigma_0 \exp \left( \frac{-E}{RT} \right)
\end{equation}
\[ \sigma = \frac{\sigma_0}{T} \exp \left( \frac{E_a}{kT} \right), \]

where \( T \) is temperature in K, \( \sigma \) is total conductivity at temperature \( T \), \( \sigma_0 \) is a pre-exponential factor, \( E_a = \Delta H_m + \Delta H_a \) is the activation energy, and \( k \) is Boltzmann constant. \( \Delta H_m \) and \( \Delta H_a \) denote the migration enthalpy and association enthalpy of the oxygen vacancy, respectively. \( \sigma_0 \) 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\(_{2}\)O\(_3\) and Sm\(_{2}\)O\(_3\) into the CeO\(_2\) system would lead to the formation of more oxygen vacancies because of the charge compensation in electrolyte materials.

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 the Ce\(_{0.9-x}\)Gd\(_{0.1}\)Sm\(_x\)O\(_{2-\delta}\) samples 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\(_x\)O\(_{2-\delta}\) (\( x = 0, 0.10 \)). 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\(_x\)O\(_{2-\delta}\) 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]:

\[ \text{Sm}_2\text{O}_3 \xrightarrow{\text{CeO}_2} 2\text{Sm}_0^x + 3\text{O}_0^x + V_{00}^0, \]

\[ \text{Gd}_2\text{O}_3 \xrightarrow{\text{CeO}_2} 2\text{Gd}_0^x + 3\text{O}_0^x + V_{00}^0. \]

The addition of Gd\(_2\)O\(_3\) and Sm\(_2\)O\(_3\) 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 $x = 0.05$.

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References