

Characterization of Sm and Nd Co-Doped Ceria-Based Electrolyte Materials

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Ceria doped with trivalent cations, such as rare earth elements, is considered to be one of the most promising electrolyte materials for intermediate-temperature solid oxide fuel cells, which are an alternative to the commercially used yttrium-stabilized zirconia (YSZ). The aim of this work research is to synthesize Sm and Nd co-doped ceria materials using the Pechini method as solid electrolyte for intermediate temperature solid oxide fuel cell. $\text{Ce}_{0.75}\text{Sm}_{0.20}\text{Nd}_{0.05}\text{O}_{1.875}$, $\text{Ce}_{0.65}\text{Sm}_{0.20}\text{Nd}_{0.15}\text{O}_{1.825}$, and $\text{Ce}_{0.60}\text{Sm}_{0.20}\text{Nd}_{0.20}\text{O}_{1.80}$ have been chosen as target of this study. Microstructural and physical properties of the samples were characterized with X-ray diffraction, scanning electron microscopy, thermogravimetric analysis methods. The results of the thermogravimetry/differential thermal analysis and X-ray diffraction indicated that a single-phase fluorite structure formed at the relatively low calcination temperature of 600 °C for 3 h. The two-probe ac impedance spectroscopy was used to study the total ionic conductivity of doped and co-doped ceria ceramics at 800 °C. The $\text{Ce}_{0.60}\text{Sm}_{0.20}\text{Nd}_{0.20}\text{O}_{1.80}$ sample showed maximum ionic conductivity.

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1. Introduction

Solid oxide fuel cells (SOFCs) have the potential as an alternative energy system in the future. Recently SOFCs have been attracting more attention due to high efficiency and clean energy. Electrolyte materials used for SOFCs are usually the main components determining the performance of the fuel cell. Yttria-stabilized zirconia (YSZ) is a standard electrolyte for conventional SOFC systems. To obtain the required level of ionic conductivity of YSZ, the operation temperatures are usually as high as 1000 °C. However, at such high operating temperatures, there are some problems such as thermal mismatch between cell components, chemical instability, etc. [1, 2]. It is thus necessary to reduce the operating temperature of SOFCs. It is known that the replacement of YSZ electrolyte by the doped ceria that has high oxide-ionic conductivity at low temperature, is one of the most promising methods for lowering the operating temperature [3]. Especially, the use of rare earth elements such as Nd, Sm and Gd as dopants for ceria improved the ionic conductivity of ceria [4–6]. To further improve conductivity of ceria based solid electrolyte materials, co-doped or double doped strategy have been used in many studies and most of them gave positive results [7–12].

In this work, $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), $\text{Ce}_{0.75}\text{Sm}_{0.2}\text{Nd}_{0.05}\text{O}_{1.875}$, $\text{Ce}_{0.65}\text{Sm}_{0.2}\text{Nd}_{0.15}\text{O}_{1.825}$, $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ samples were synthesized by simple Pechini method. The effect of the co-doping element on

structural properties and ionic conductivity was compared to singly-doped ceria (denoted as samarium-doped ceria for singular doping). The aim was to develop new ceria-based electrolyte materials to further improve the ionic conductivity. Microstructural and physical properties of the samples were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), the Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG) analysis methods. Furthermore, the co-dopant effects on the ionic conductivity of the ceria based electrolytes were investigated.

2. Materials and method

Cerium nitrate [$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, purity 99.999%, Sigma Aldrich], samarium nitrate [$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, purity 99.999%, Sigma Aldrich], and neodymium nitrate [$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, purity 99.999%, Sigma Aldrich] were used as the starting materials. In order to prepare $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.75}\text{Sm}_{0.2}\text{Nd}_{0.05}\text{O}_{1.875}$, $\text{Ce}_{0.65}\text{Sm}_{0.2}\text{Nd}_{0.15}\text{O}_{1.825}$, $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ electrolyte samples, the nitrates were weighed and dissolved in the de-ionized water with the desired concentrations. Citric acid (anhydrous citric acid, Boehringer Ingelheim) was dissolved in de-ionized water and then was added with ethylene glycol (R.P. Normopur) to the cation solution. The molar ratio of total oxide (TO): citric acid (CA) and ethylene glycol: citric acid was selected as 2:1, 4:1, respectively. The obtained purple solutions were heated and stirred on a hot plate at 85 °C. With the evaporation of water, the solution was gradually transformed into a brown viscous gel. The gel was placed in an oven at 110 °C for 24 h until it changed into a dark brown loose foam. Afterwards, the foam was

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placed in a furnace for further heating until autoignition of the foam took place and light green powders were produced. The powders were collected and calcined at 600 °C for 3 h to remove the carbon residue. The calcined powders were uniaxially pressed at a compaction pressure of 200 MPa into 10 mm diameter pellets and sintering was performed at 1400 °C for 6 h.

Thermochemical properties of the dried loose foam were investigated by thermogravimetry/differential thermal analysis (DTA) (SII Exstar 6000 TG/DTA 6300) in the temperature range of 25–700 °C at a heating rate of 5 °C/min in air.

The X-ray spectra of Sm and Nd co-doped ceria particles were obtained over the 2θ range of 10–90° by using Rigaku D/max-2200 ultima X-ray diffractometer with Cu K_α radiation (1.5406 Å). The FT-IR spectra were recorded with a Perkin Elmer Spectrum 100 instrument. FEIQUANTA FEG 450 scanning electron microscope was used to study the morphology and microstructure of the sintered samples. The elemental distribution of the sintered samples was also investigated by the energy dispersive X-ray spectroscopy (EDS), and the mapping images were obtained by scanning 32 frames. Impedance measurements (electrochemical impedance spectroscopy (EIS)) were taken by using SOLARTRON 1260 FRA and 1296 interface at 800 °C in air atmosphere.

3. Results and discussion

3.1. Thermal analysis

The conversion of the so-prepared amorphous precursors into crystalline samarium-doped ceria was achieved by heating the dried solids at a heating rate of 5 °C min⁻¹ to 600 °C and keeping them at this temperature for 3 h. Figure 1 shows the simultaneous TGA/DTA curves of the dried Ce_{0.75}Sm_{0.20}Nd_{0.05}O_{1.875} foam. The TG curve displays a minor weight-loss of 4.15% between 27 and 170 °C which may be attributed to the water loss associated with foam. A strong exothermic peak in DTA curve along with a maximum weight loss of 55.2% that occurred at approximately 220 °C, may be due to the combustion of organic residues and the gradual crystallization of Ce_{0.75}Sm_{0.20}Nd_{0.05}O_{1.875}. The foam was observed to produce a self-sustained flame when it was kept in an oven at 220 °C. It is evident that this is the temperature for a vigorous combustion reaction of Sm-Nd-doped ceria-containing nitrate oxidant system.

No remarkable change can be seen at above in the TGA/DTA curves. This proves that Ce_{0.75}Sm_{0.20}Nd_{0.05}O_{1.875} has been almost perfectly crystallized beyond this temperature.

3.2. X-ray analysis

Figure 2a shows the XRD patterns of the synthesized Ce_{0.8}Sm_{0.2}O_{1.9}, Ce_{0.75}Sm_{0.2}Nd_{0.05}O_{1.875}, Ce_{0.65}Sm_{0.2}Nd_{0.15}O_{1.825}, Ce_{0.6}Sm_{0.2}Nd_{0.2}O_{1.8} powders after calcination at 600 °C for 3 h. It can be clearly seen that all powders were single-phased with a cubic fluorite structure (JCPDS powder diffraction file no. 34-0394).

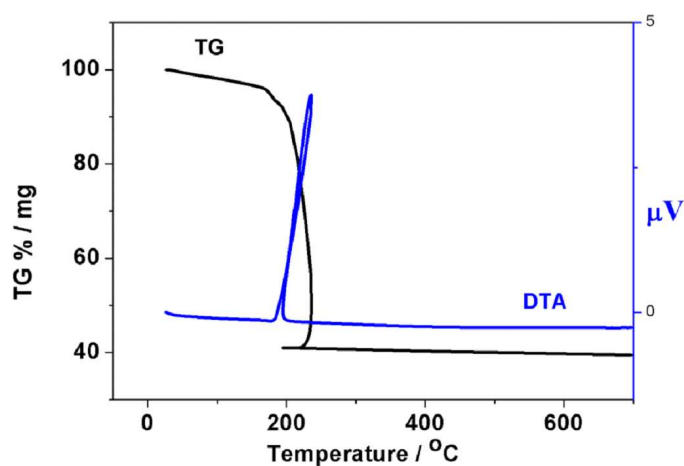


Fig. 1. TG–DTA curves of thermal decomposition of Ce_{0.75}Sm_{0.20}Nd_{0.05}O_{1.875} powder precursors at a heating rate of 5 °C min⁻¹ in static air.

No other peaks attributed to impurities or other phases, Sm₂O₃ or Nd₂O₃, were detected. Thus, single fluorite-phased Ce_{0.8}Sm_{0.2}O_{1.9}, Ce_{0.75}Sm_{0.2}Nd_{0.05}O_{1.875}, Ce_{0.65}Sm_{0.2}Nd_{0.15}O_{1.825}, Ce_{0.6}Sm_{0.2}Nd_{0.2}O_{1.8} powders can be synthesized successfully using the Pechini method.

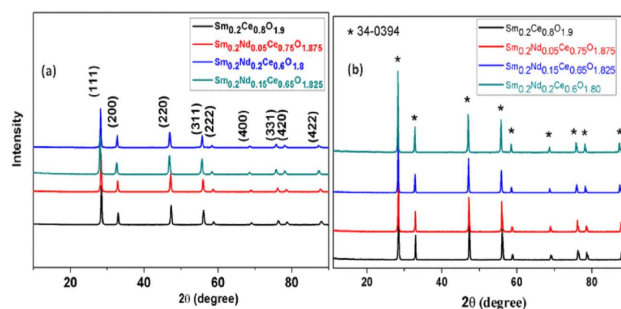


Fig. 2. X-ray diffraction patterns of the synthesized Ce_{0.8}Sm_{0.2}O_{1.9}, Ce_{0.75}Sm_{0.2}Nd_{0.05}O_{1.875}, Ce_{0.65}Sm_{0.2}Nd_{0.15}O_{1.825}, Ce_{0.6}Sm_{0.2}Nd_{0.2}O_{1.8} powders after (a) calcination at 600 °C for 3 h, (b) sintering at 1400 °C for 6 h.

It can also be seen from XRD patterns that during powder combustion, Sm³⁺ and Nd³⁺ co-doped ceria electrolytes are formed by substituting Ce⁴⁺ with doping elements Sm³⁺ and Nd³⁺; therefore, a complete solid solution may be formed. The broad peaks shown in Fig. 2a indicate the existence of nanosized crystallites formed during the calcination process. From the X-ray diffractograms, the crystallite size, D , is calculated from well-known Scherrer's formula

$$D = K\lambda/(\beta \cos \theta), \quad (1)$$

where D is the crystallite size (nm), K is the constant taken as 0.9, λ is wavelength of radiation (0.154056 nm for Cu K_α), β is the corrected peak at full width at half maximum (FWHM) intensity and θ is the scattering angle of the main reflection (111). The av-

erage crystallite size (D) of all crystallite powders was between 54 and 62 nm. The co-doping of rare-earth oxides into CeO_2 can cause a small shift in the ceria peaks. Figure 2b displays the XRD patterns of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.75}\text{Sm}_{0.2}\text{Nd}_{0.05}\text{O}_{1.875}$, $\text{Ce}_{0.65}\text{Sm}_{0.2}\text{Nd}_{0.15}\text{O}_{1.825}$, $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ pellets after sintering of powders at 1400°C for 6 h. It can be observed that the peaks shift to lower 2θ values on increasing the amount of the Nd dopant. The ionic radii of Sm^{3+} , Nd^{3+} , and Ce^{4+} decrease in the order $r_{\text{Nd}^{3+}} > r_{\text{Sm}^{3+}} > r_{\text{Ce}^{4+}}$; thus, with more substitution of Ce^{4+} with increasing Nd^{3+} , the volume of the CeO_2 unit cell will be further enlarged and may result in a peak shifting towards lower 2θ values.

3.3. FTIR analysis

Figure 3 displays FTIR spectral features of Sm and Nd co-doped ceria samples. The broad band of weak intensity occurring in the range $3500\text{--}3400\text{ cm}^{-1}$ is due to the O–H stretching vibration of the OH groups. The weak bands at $\approx 1070\text{ cm}^{-1}$ correspond to the ν (O–H) mode of (H-bonded) water molecules and δ (OH), respectively.

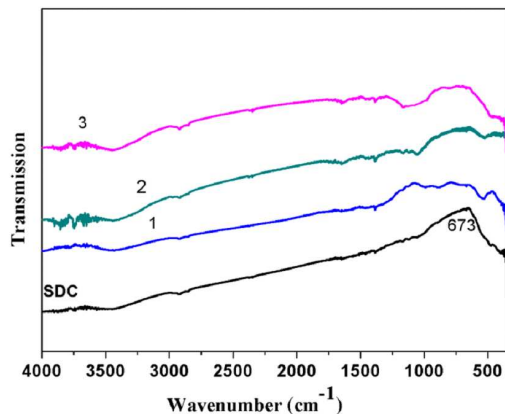


Fig. 3. FTIR spectra of the calcined SDC, 1: $\text{Ce}_{0.75}\text{Sm}_{0.2}\text{Nd}_{0.05}\text{O}_{1.875}$, 2: $\text{Ce}_{0.65}\text{Sm}_{0.2}\text{Nd}_{0.15}\text{O}_{1.825}$ and 3: $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ powders at 600°C for 3 h.

KBr pellets containing sample were used in FTIR measurements. The water peak at ≈ 3400 and 1070 is due to the moisture in KBr. (The finely powdered potassium bromide absorbs more humidity (it is hygroscopic) from air during sample preparation.) The FTIR spectrum of the Sm and Nd co-doped ceria also exhibits strong broad band at $700\text{--}360\text{ cm}^{-1}$ which are attributed to the characteristic Ce–O vibrations [13, 14].

3.4. Microstructure

The micro-structures of the SDC pellets sintered at 1400°C for 6 h with different neodymium doping are compared in Fig. 4.

As seen from SEM images (Fig. 4), all samples are nearly fully dense with very few residual pores. There

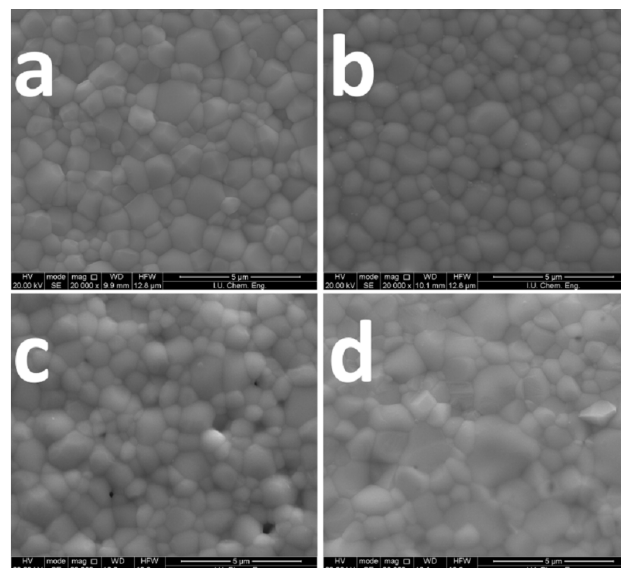


Fig. 4. Scanning electron micrographs of sintered (a) $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$, (b) $\text{Ce}_{0.75}\text{Sm}_{0.2}\text{Nd}_{0.05}\text{O}_{1.875}$, (c) $\text{Ce}_{0.65}\text{Sm}_{0.2}\text{Nd}_{0.15}\text{O}_{1.825}$, (d) $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ ($20,000\times$).

is no exaggerated grain growth and the average particle size observed from micrographs is approximately $1\ \mu\text{m}$ for $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.75}\text{Sm}_{0.2}\text{Nd}_{0.05}\text{O}_{1.875}$, $\text{Ce}_{0.65}\text{Sm}_{0.2}\text{Nd}_{0.15}\text{O}_{1.825}$. However, the average particle size increased to $1.16\ \mu\text{m}$ for the sample $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$. No significant effect of Nd addition on the microstructure of the samarium doped ceria was observed. SEM–EDS map analyses were performed on the outer surface of $\text{Ce}_{0.60}\text{Sm}_{0.20}\text{Nd}_{0.20}\text{O}_{1.80}$ sample which is given in Fig. 5. As can be seen, Ce, Sm, and Nd are homogeneously dispersed in the structure. The calculated relative densities for $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.75}\text{Sm}_{0.2}\text{Nd}_{0.05}\text{O}_{1.875}$, $\text{Ce}_{0.65}\text{Sm}_{0.2}\text{Nd}_{0.15}\text{O}_{1.825}$ are approximately 90% of the theoretical value. On the other hand, $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ sample had the highest density of 95% which suggests that it was the compact one.



Fig. 5. SEM–EDS map analyses for $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.80}$ sample.

3.5. Conductivity measurement

The ionic conductivity measurement was performed in air at 800°C . A complex plane plot of real impedance, Z' , versus imaginary impedance, Z'' , was prepared for each set of data. By curve fitting a circle to semicircles on these plots, sample resistances ($R_{\text{total}} = R_{\text{gi}} + R_{\text{gb}}$) were obtained [15]. The total conductivity (σ_{T}) values were then calculated using the equation

$$\sigma_T = \frac{l}{AR_{\text{total}}}, \quad (2)$$

where l is the thickness, A is the cross-sectional area of the sample. Figure 6 shows the complex impedance spectra plots of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ and $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ samples at 800 °C.

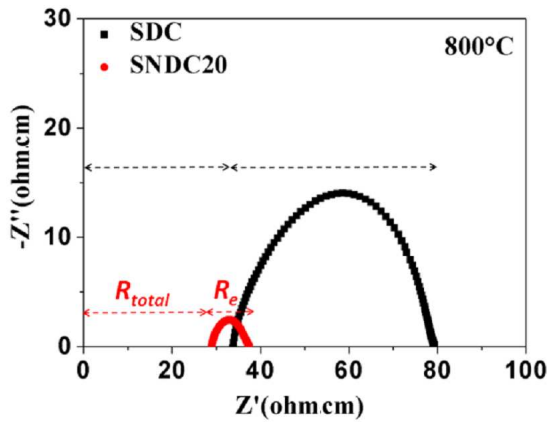


Fig. 6. Complex impedance spectra plots of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) and $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ (SNDC20) pellets sintered at 1400 °C, measured at 800 °C in air. The total resistance (R_{total}) and electrode contributions are represented as R_{total} , R_e , respectively.

According to the electrochemical impedance spectroscopy results, $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.80}$ exhibited a total conductivity of $3.50 \times 10^{-2} \text{ S cm}^{-1}$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ showed a total conductivity of $2.95 \times 10^{-2} \text{ S cm}^{-1}$ at 800 °C. Neodymium co-dopants improved the electrical conductivity of Sm-doped ceria by $\approx 20\%$.

4. Conclusions

$\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$, $\text{Ce}_{0.75}\text{Sm}_{0.2}\text{Nd}_{0.05}\text{O}_{1.875}$, $\text{Ce}_{0.65}\text{Sm}_{0.2}\text{Nd}_{0.15}\text{O}_{1.825}$, $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ powders were successfully synthesized by the Pechini method, using their corresponding metal nitrates as oxidizers and citric acid as a combustion fuel. All the electrolyte samples were found to be fluorite-type ceria based solid solutions, which were formed in the calcination process at 600 °C and crystallized better in the sintering process at 1400 °C. $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.80}$ sample had good sinterability at 1400 °C, giving relative high density of 95% and grain size of about 1.16 μm . According to SEM results, no significant effect of Nd addition on the micro-structure of the samarium doped ceria was observed. Co-dopants improved the electrical conductivity of Sm-doped ceria, and thus, there is a significant potential for the use of $\text{Ce}_{0.6}\text{Sm}_{0.2}\text{Nd}_{0.2}\text{O}_{1.8}$ electrolyte material for the intermediate temperature SOFCs.

Acknowledgments

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