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# Synthesis and characterizations of $Ce_{0.85}(Sm_xNd_{1-x})_{0.15}O_{2-\delta}$ ceramics

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ABSTRACT

$Sm^{3+}$ and $Nd^{3+}$ co-doped ceria, $Ce_{0.85}(Sm_xNd_{1-x})_{0.15}O_{2-\delta}$ (SNDC) ($x$ = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) was synthesized using the urea nitrate combustion method. The synthesized powders showed the single phase of a fluorite-type structure. The SNDC were sintered to over 98% of their theoretical density at1450 °C for 4 h in air. The electrical properties of these ceramics were investigated in both oxidizing (air) and reducing atmospheres (25 mol% $H_2$ and 75 mol% $N_2$). $Ce_{0.85}(Sm_{0.6}Nd_{0.4})_{0.15}O_{2-\delta}$ (SNDC ($x$ = 0.6)) had the highest conductivity and the lowest activation energy in air, with the values of 0.018 S $cm^{-1}$ and 0.527 eV at 550 °C, respectively. Furthermore, in reducing atmosphere, the SNDC ($x$ = 0.6) showed the slowest oxygen surface exchange. In addition, characterization of SNDC at the actual solid oxide fuel cell (SOFC) operation conditions indicated that co-doped ceria materials had larger transference number of oxygen ions than singly doped ones. And among them, the SNDC ($x$ = 0.6) had the largest value. Therefore, the ratio of $Sm^{3+}$ to $Nd^{3+}$ does have significant effect on the electrical properties of SNDC. And the SNDC with $x$ = 0.6 is supposed to be the optimum composition.



## 1. Introduction

Since the expansion of global industries is causing the consumption of increasing amounts of energy, exploring new energy sources has become an important issue. Among the various new power resource candidates, SOFC has attracted considerable interest due to its advantages: (1) high energy conversion efficiency; (2) fuel flexibility; (3) low emission of pollutants [1–3]. And yttria-stabilized zirconia (YSZ) is widely used as an electrolyte material in SOFC that operates above 800 °C [4]. However, the SOFC operating at high temperatures requires specialized fuel cell interconnection and insulation materials, as well as much time and energy to heat up to its operating temperatures [5]. This makes the commercialization of SOFC difficult (shortening the lifetime and increasing the fabrication cost). Therefore, many researchers have focused on reducing the operation temperatures of SOFC down to intermediate temperatures (600–800 °C) or even low temperatures ((300–600 °C)) [1,6–10]. Due to the much higher ohmic resistance of the electrolyte (compared to other components in SOFC single cells) at lower temperatures, finding highly ionic conductive electrolyte compositions and novel structures of electrolyte has been important in fabricating highly efficient SOFC that works at lower temperatures. Furthermore, decreasing the thickness of the electrolyte and using highly ionic-conductive materials as electrolyte are thought to be viable to fabricate intermediate-temperature SOFC [3].

Reportedly, a solid oxide electrolyte with high ionic conductivity is effective indeed in developing intermediate-temperature (IT) SOFC [5,6]. Over the last 30 years, doped ceria (DCO) materials have been one kind of popular electrolyte materials because of their higher ionic conductivity. In addition, $Gd^{3+}$ or $Sm^{3+}$ singly doped ceria was found to have the highest ionic conductivity among all singly doped ceria materials [1,11,12]. However, the reduction of $Ce^{4+}$ to $Ce^{3+}$ forces this group of electrolyte materials to exhibit mixed ionic–electronic conductivity in reducing atmospheres or at high temperatures, resulting in the voltage-decreasing and performance diminishment of cells [13,14]. Fortunately, the application of co- or multi-dopant which can enhance ionic conductivity is one of the feasible methods to tackle this issue [15,16]. Herle et al. discovered that co-doped ceria with multiple dopants showed much higher ionic conductivity in air than even the best singly doped ceria [17]. Besides, Andersson et al. indicated that $Nd^{3+}/Sm^{3+}$ or $Pr^{3+}/Gd^{3+}$ co-doped ceria had the highest conductivity compared to other co-doping pairs [18]. This has since been verified experimentally by Omar et al. [19,20] and Liu et al. [21]. Undoubtedly, co-doped ceria materials based on $Sm^{3+}$ and

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$Nd^{3+}$ has the potential to be one viable electrolyte candidate for SOFC working at lower temperatures.

Several researchers have investigated the effect of co-doping on the properties of ceria based materials. Shobit Omar et al. and Bin Li et al. reported the electrical properties of $Ce_{1-x}Sm_{x/2}Nd_{x/2}O_{2-\delta}$ with different $x$ values, finding that $Ce_{0.85}Sm_{0.075}Nd_{0.075}O_{2-\delta}$ had a 30% higher grain ionic conductivity ($1.0 \times 10^{-2}$ S cm$^{-1}$ at 550 °C) than $Gd_{0.10}Ce_{0.90}O_{2-\delta}$ (GDC) at 550 °C in air [4,22]. Subsequently, Zhan Gao et al. compared the properties of $Ce_{0.85}Sm_{0.075}Nd_{0.075}O_{2-\delta}$ synthesized by different methods, and found that the oxalate co-precipitation was the best method to synthesize $Ce_{0.85}Sm_{0.075}Nd_{0.075}O_{2-\delta}$ (compared to the other three processes of polyvinyl alcohol-assisted sol–gel, citrate sol–gel, and polyethylene glycol-assisted sol–gel) [23]. Furthermore, one SOFC single cell fabricated with $Ce_{0.85}Sm_{0.075}Nd_{0.075}O_{2-\delta}$ electrolyte showed a maximum power density of 1.43 W cm$^{-2}$ and a specific area resistance of 0.033 Ω cm$^2$ at 650 °C [6]. However, not enough work has been conducted on $Ce_d(Sm_xNd_{1-x})_{1-d}O_{2-\delta}$ (where $d$ is a constant, while $x$ is a variable) to find an optimum ratio of $Sm^{3+}$ concentration to $Nd^{3+}$. Besides, attempting to synthesize $Sm^{3+}$ and $Nd^{3+}$ co-doped ceria powder using a combustion method (a method frequently utilized to synthesize fine powders), is meaningful as well, because this method has not been used yet to produce ceria based co-doping powders publicly. Not only the conductivity in air, but also the electrical properties in reducing atmosphere and at the actual SOFCs operation conditions should be investigated.

In this work, the electrical properties of $Ce_{0.85}(Sm_xNd_{1-x})_{0.15}O_{2-\delta}$ ($x$ = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) were studied by analyzing the electrical properties in both oxidizing (air) and reducing (25 mol% $H_2$ and 75 mol% $N_2$) atmosphere. In addition, the effect of the $x$ value on the oxygen surface exchange of SNDC was investigated as well in reducing atmosphere. Finally, by measuring the performance of identically structured SOFC single cells, transference number of oxygen ions of SNDC was studied. Based on characterizations and analysis, the optimum $x$ value for $Ce_{0.85}(Sm_xNd_{1-x})_{0.15}O_{2-\delta}$ was anticipated to be found among the six candidates (0.0, 0.2, 0.4, 0.6, 0.8 and 1.0).

## 2. Experimental

$Ce(NO_3)_3{\cdot}6H_2O$ (99.5%, Alfa Aesar), $Sm(NO_3)_3{\cdot}6H_2O$ (99.9%, Alfa Aesar), $Nd(NO_3)_3{\cdot}6H_2O$ (99.9%, Strem Chemicals), and $CO(NH_2)_2$ (⩾99%, Samkun) were used as raw materials to synthesize the SNDC powder. The nitrates were weighed according to the compositions ($Ce_{0.85}(Nd_{1-x}Sm_x)_{0.15}O_{2-\delta}$ ($x$ = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0)) and the mole ratio of urea to total metal cation was determined to be 3.0 [24]. These raw materials were then dissolved in deionized water and subsequently stirred for around half an hour until the formation of a transparent solution. Finally, the solution was heated on a hot plate until spontaneous combustion occurred. The ash was ball-milled for 24 h with ethanol and zirconia balls in a polyethylene bottle and then dried. The dried SNDC powder was calcined at 900 °C for 2 h and subsequently ground again for 24 h using a ball mill. The as-prepared SNDC powder was pressed into bars (40 mm × 4 mm × 4 mm) and discs (10 mm in diameter and 1 mm in thickness) under a pressure of 100 MPa, and then sintered at 1450°C for 4 h in air.

Phase identification of both calcined and sintered SNDC was carried out using a Rigaku D/MAX-111A X-ray diffractometer (XRD) with Cu Kα radiation. The lattice parameter was calculated using the following steps: measuring the XRD pattern of the NBS silicon standard specimen to obtain the system error of the XRD machine in the lab with the step size of 0.25°; calibrating the diffraction angle of each peak in the XRD patterns of SNDC; calculating the lattice parameter using the following formulas:

$$2d\sin\theta = \lambda \tag{1}$$

$$d = \frac{\alpha}{\sqrt{h^2 + k^2 + l^2}} \tag{2}$$

where $\lambda$ is the wavelength of the X-ray, $\theta$ is the incident angle, $d$ is the spacing of the crystal planes ($h$, $k$, $l$), and $\alpha$ is a lattice parameter. The theoretical density of each composition was then calculated with the lattice parameter. The reduction degree was evaluated by a simple qualitative comparison of the conductivities being measured in air and the reducing atmosphere. In addition, the actual density of the sintered SNDC was measured via Archimedes method. Then the morphology of the powder and microstructure of the sintered body were observed using a Hitachi-4700 field emission scanning electron microscope (FESEM).

The conductivity of SNDC was measured using four-probe method in air, from 800 to 300 °C. The gold paste was brushed on the specimens, being used as electrode. Then in order to study the effect of co-doping on the oxygen surface exchange, the conductivity of SNDC was continually measured for 250 min at 650 °C in reducing atmosphere which consisted of 25 mol% $H_2$ and 75 mol% $N_2$. Finally, oxygen concentration cells (Pt/$Ce_{0.85}(Sm_xNd_{1-x})_{0.15}O_{2-\delta}$/Pt) were used to achieve the transference number of oxygen ions of SNDC. The preparation steps of cells are following: pressing each batch of 6 g of SNDC powder into disks with the diameter of 36 mm, calcining the green disks at 900 °C for 3 h, polishing the disks to be 1.5 mm, brushing the Pt paste onto both sides of the disks, calcining the specimens in air at 900 °C for 45 min. And the theoretical voltage ($E_T$) is given by a following equation [25]:

$$E_T = E^0 - (2.304 \times 10^{-4}\ \text{V/K})(T - T_0) \tag{3}$$

where $E^0$ is the standard-state reversible voltage (1.23 V, to $H_2$–$O_2$ fuel cell). $T_0$ and $T$ represent the temperature at the standard state and the temperature at measurement condition, respectively. And the transference number of oxygen ions is presented by another following equation:

$$t_i = E_{means}/E_T \tag{4}$$

where $E_{means}$ means the open circuit voltage (OCV). In this work, the OCV of oxygen concentration cells was measured from 600 to 400 °C with a gas flow rate of 200 cm$^3$ min$^{-1}$. The schematic diagram of the single cell measurement set-up has been given in one of our previous papers [26].

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns of the calcined SNDC powder. Each of the six compositions has the single phase of a fluorite-type structure. And peaks of XRD pattern shift to higher angles with increasing amount of $Sm^{3+}$ (corresponding decrease in $Nd^{3+}$

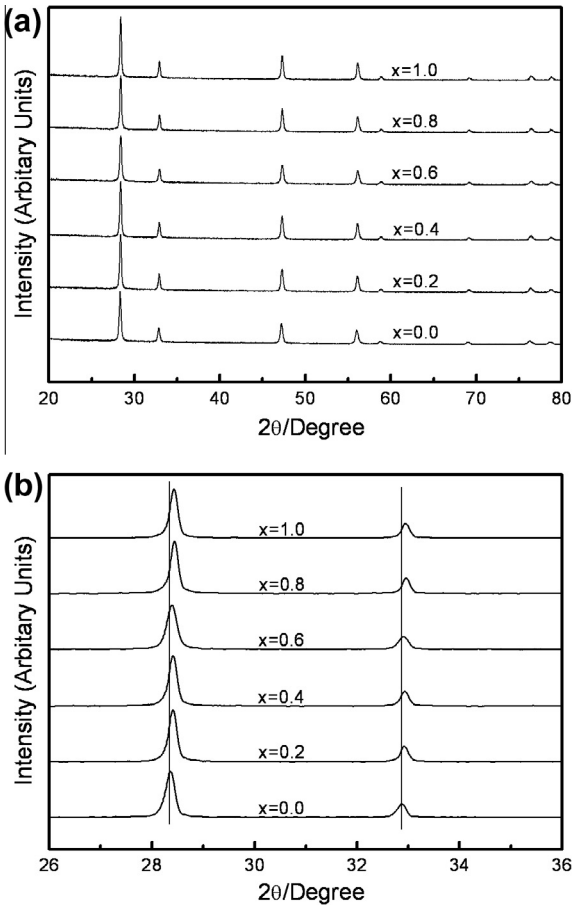


**Fig. 1.** (a) XRD pattern and (b) partly enlarged XRD pattern of calcined SNDC.