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Characterization of NGCO-LSCF composite SOFC cathodes using electrochemical impedance spectroscopy

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Abstract

In this study, a co-dopant gadolinium-doped ceria (GCO) was synthesized to produce more efficient cathode materials for intermediate temperature solid oxide fuel cell (IT-SOFC). The neodymium (Nd) was co-doped with GCO in four different weight ratios in the formula $\text{Nd}_x\text{Gd}_{0.15}\text{Ce}_{0.85-x}\text{O}_{2-\delta}$ (NGCO); the selected percentages for x were 1%, 3%, 5% and 7%. The XRD

patterns showed pure phase for all synthesized compositions and good compatibility at high temperature under static air with the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{2-\delta}$ (LSCF) most common ceramic cathode material in IT-SOFC. Impedance spectroscopic of symmetrical cells of the composites NGCO-LSCF in the temperature range 650 °C to 800 °C in steps of 50 °C and a frequency range of 0.1 to 1 MHz in synthetic air has revealed interesting results. The lowest polarization resistance, R_p , was achieved for $\text{Nd}_{0.05}\text{Gd}_{0.15}\text{Ce}_{0.80}\text{O}_{2-\delta}$ ($0.06 \Omega \text{ cm}^2$ at 800 °C, $0.17 \Omega \text{ cm}^2$ at 750 °C, $0.31 \Omega \text{ cm}^2$ at 700 °C, and $0.59 \Omega \text{ cm}^2$ at 650 °C). The expected high increase in R_p was not observed for the sample with higher Nd content (7 % Nd). Thus, it can be said that there is a distinction between the compositions $\text{Nd}_{0.05}\text{Gd}_{0.15}\text{Ce}_{0.80}\text{O}_{2-\delta}$ and $\text{Nd}_{0.07}\text{Gd}_{0.15}\text{Ce}_{0.78}\text{O}_{2-\delta}$; the co-doping of Nd in NGCO incremented the oxygen ion diffusion path, thereby optimization in the triple phase boundary (TPB) sites was obtained. Furthermore, SEM and TGA measurements were conducted to clarify the reasons of such improvements. This work showed that an NGCO-LSCF composite can be considered as a potential candidate for cathode material for future IT-SOFC applications.

Keywords: IT- SOFC, co-precipitation method, cathode material, Co-doped ceria, Impedance spectroscopy, Polarization resistance

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted a lot of interest since they convert chemical energy of hydrogen or hydrocarbon based fuels to electrical energy directly at high efficiency and with no emission of atmospheric pollutants, apart from water and carbon dioxide. The electrical energy produced can be used for powering vehicles or driving electrical machinery or appliances. This technology has an important drawback, though: the high operating temperature implies higher degradation of the various components over time, thus hindering commercialization of this technology at a large scale [1, 2]. Therefore, continuous research is being carried out to improve the material and component characteristics, such as compatibility with interconnects and supporting structure, mechanical and chemical stability, high electronic and ionic conductivity, lower polarization resistance and improved performance at intermediate temperatures [3, 4].

Ceria (CeO_2) is a prominent example of such materials development. It is readily available in the chemicals market and can be synthesized both in small and in large quantities following fast, easy, and low-cost methods of synthesis. Furthermore, it can be easily modified by doping with rare-earth or other elements to supply promising properties suitable for SOFC, oxygen sensor, or electrolysis applications [5-7]. Gadolinium-doped ceria (GCO) is a well known derivate of ceria and has been reported as one of the key ionic conductive electrolyte materials for SOFC [8]. Moreover, GCO also exhibits significant electronic conductivity due to the reduction of Ce^{4+} to Ce^{3+} under low pressure and high temperature [9]. However, the generated electronic conductivity may lead to a decrease in the power density of the cell, as well as affect the

mechanical stability [10]. To overcome such limitation, co-doping with rare earth elements has proven to be effective [11], such as $\text{Ce}_{1-x-y}\text{Sm}_x\text{Ca}_y\text{O}_{2-\delta}$, $\text{Ce}_{1-x-y}\text{La}_x\text{Sr}_y\text{O}_{2-\delta}$, $\text{Ce}_{1-x-y}\text{Gd}_x\text{Pr}_y\text{O}_{2-\delta}$, $\text{Ce}_{1-x-y}\text{Sm}_x\text{Gd}_y\text{O}_{2-\delta}$, and others [12-16].

In recent years, the perovskite oxide $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) has been extensively investigated as SOFC cathode material due to its mixed electronic and ionic conductivity [17-20]. Moreover, LSCF is chemically and mechanically compatible with doped ceria electrolytes [21]. In order to increase the triple phase boundary (TPB) and, consequently, to produce more efficient cathodes, several research groups have conducted work to analyze the effect of combining electrolyte materials with LSCF (co-doped ceria-LSCF composite) [22]. Similar to GCO-LSCF the NCGO-LSCF composite allows profound oxygen exchange over the electrode surface to retain appreciable amounts of ionic and electronic conductivity at intermediate temperatures [23]. Furthermore, the porous microstructure of the composite cathode also plays a significant role in improving the cathode performance [21, 24] .

In this study, an NGCO-LSCF composite material was prepared by varying the Nd weight ratio in the GCO matrix as a co-dopant. Electrochemical impedance spectroscopy was used to understand the effect of Nd on the polarization resistance. Moreover, SEM and TGA measurements were carried out to understand the factors that reduced the R_p of the NGCO-LSCF composites.

2. Experimental

2.1. Material preparation

Neodymium (Nd) and gadolinium (Gd) co-doped ceria ($\text{Nd}_x\text{Gd}_{0.15}\text{Ce}_{0.85-x}\text{O}_{2-\delta}$, NGCO) was prepared by a co-precipitation method using $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ raw materials (Sigma Aldrich). Stoichiometric amounts of high-purity (99.9%) powders were dissolved in de-ionized (DI) water to form a 0.1 M solution in such a way that the amount of Gd remained invariant and the weight ratio of Nd and Ce was adjusted to 1:84, 3:82, 5:80, and 7:78 for $\text{Nd}_{0.01}\text{Gd}_{0.15}\text{Ce}_{0.84}\text{O}_{2-\delta}$, $\text{Nd}_{0.03}\text{Gd}_{0.15}\text{Ce}_{0.82}\text{O}_{2-\delta}$, $\text{Nd}_{0.05}\text{Gd}_{0.15}\text{Ce}_{0.80}\text{O}_{2-\delta}$ and $\text{Nd}_{0.07}\text{Gd}_{0.15}\text{Ce}_{0.78}\text{O}_{2-\delta}$, respectively. The mixture was placed on a hot plate and stirred for 30 min at 85 °C. Then, a solution of 0.2 M sodium carbonate (Na_2CO_3) was added as co-precipitating agent to the nitrate solution until the pH approached 10. The solution was stirred until the formation of a white precipitate, washed with DI water repeatedly to remove unreacted nitrates and vacuum filtered, followed by drying in an oven at 80 °C for 12 h. The dried sample was calcined at 800°C for 4 h and ground manually using an agate mortar and pestle to obtain a homogenous and fine $\text{Nd}_x\text{Gd}_{0.15}\text{Ce}_{0.85-x}\text{O}_{2-\delta}$ (NGCO) powder.

Commercial powder of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{2-\delta}$ (LSCF, Sigma Aldrich, 99.9% pure) was mixed with the synthesized NGCO (mass ratio 50:50) to confirm the compatibility at high temperature.

2.2. Material characterization

Powder X-ray diffractogram were collected with an XPert³ Malvern Panalytical diffractometer using $\text{CuK}_{\alpha 1}$ radiation in the range 2θ (°) = 20 to 80 in steps of 0.035° at 0.023333 s

per step. The technique was used to characterize the purity of the synthesized phases (NGCO) and to analyze the stability with one of the most researched cathode materials ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{2-\delta}$) for IT-SOFC at high temperature. Using the Scherer formula, the average crystallite size was calculated from the diffractogram as

$$\text{crystallite size} = \frac{k\lambda}{d\cos\theta} \quad (1)$$

Whereas, k is the crystal shape factor ($k= 0.90$), the wavelength is $\lambda=15.406$ nm, d is the full peak width at half maximum, and θ is the angle in radians.

Both the surface and the cross-section morphology of electrodes were examined with a JEOL JSM-IT100 scanning electron microscope (SEM) with an accelerating voltage of 10 to 20 kV, depending on the needs. In order to measure the mass loss of samples during the reduction, thermal gravimetric analysis (TGA) was carried out for different powders with a TA Q500 under 5 % H_2/Ar at 900 °C for 4 h, setting 1 °C min^{-1} as a heating-cooling ramp rate.

2.3. Symmetrical cell fabrication and electrochemical impedance measurement

To fabricate symmetrical cells, commercial powder of $\text{Gd}_{0.20}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (GCO20, Sigma Aldrich) was chosen as the electrolyte material. The GCO20 powder was uniaxially pressed to green pellets of 15 mm diameter and 1.3 mm thickness by applying 4 kpsi pressure. Later, the pellets were sintered at 1400 °C for 4 h in a muffle furnace under static air with a heating-cooling ramp rate of 5 °C min^{-1} . After sintering, the pellet thickness had reduced to approximately 1 mm

after polishing in the presence of alumina paste; subsequently, to remove any possible contamination, a cleaning was done by ultrasonic bath in ethanol for 30 min.

The terpineol solvent was added to the mixture NCGO-LSCF to prepare the electrode paste; the microstructure of the electrode was analyzed for different ratios between the composite and the terpineol (1:0.5, 1:1 and 2:1, respectively). The better porosity was found for the ratio 1:1. The paste was then brush-painted onto both sides of the pellet and dried at room temperature. After drying, the cell was co-fired at 1100 °C for 4 h with a heating-cooling ramp rate of 5 °C min⁻¹. Silver paste with an effective electrode area of 0.6 cm² in combination with highly conductive silver wires were mounted as current collectors. The symmetrical cell was carefully placed into a vertical alumina reactor in a vertical tubular furnace. Impedance spectroscopy measurements were conducted using a Solartron 1260 frequency analyzer. The cathode polarization resistances were measured in the 0.1 to 1MHz frequency range using an AC amplitude of 100 mA from 600 to 800 °C each 50 °C. The selected pure oxygen gas flow was 150 ml min⁻¹.

3. Results and discussion

3.1. Phase analysis and chemical compatibility

The room temperature powder X-ray diffraction patterns of the pure phases based on the formula $\text{Nd}_x\text{Gd}_{0.15}\text{Ce}_{0.85-x}\text{O}_{2-\delta}$ ($x = 0.01, 0.03, 0.05$ and 0.07) are shown in Fig. 1. Both the intensities of the peaks and the corresponding d-values were verified as a cubic fluorite with space group Fm-3m in agreement with the standard structure of CeO_2 (Coll. Code to ICSD 258058 from ICSD database). No impurities corresponding to Nd oxide or Gd oxide were detected in the

diffractogram ($N_x\text{GCO}$), which indicated that the cations were successfully incorporated in the crystal lattice. The average crystallite size of calcined NGCO at 800 °C was found to be in the range of 21 to 47 nm.

Fig. 1. XRD patterns recorded for as-prepared powder of the family of compounds $\text{Nd}_x\text{Gd}_{0.15}\text{Ce}_{0.85-x}\text{O}_{2-d}$ ($x=0.01, 0.03, 0.05$ and 0.07)

In addition, it could be confirmed that the new synthesized phases showed good chemical compatibility with the cathode material LSCF up to 1100 °C over 4 h in synthetic air (Fig. 2). Neither additional nor missing peaks were found in the X-ray diffraction pattern, which meant that the inclusion of Nd in the crystal did not affect the high stability of the double co-doped ceria.

3.2. SEM analysis

The cross-sectional analysis showed good adhesion between the dense electrolyte and the porous electrode (Fig. 3); this meant that the polarization resistances from the contact between the different layers of the cell could be expected to be insignificant. Moreover, in the representative micrographs, the thicknesses of the electrodes were above 100 μm . This parameter can as well affect R_p values negatively.

The porous surface of the electrodes was analyzed in Fig. 4. It can be seen that the porosity declined in the series; clear dense areas were shown for those samples with higher content in Nd ($\text{Nd}_{0.05}\text{Gd}_{0.15}\text{Ce}_{0.80}\text{O}_{2-\delta}$ and $\text{Nd}_{0.07}\text{Gd}_{0.15}\text{Ce}_{0.78}\text{O}_{2-\delta}$). Surprisingly, as it will be explained later, the best and the worst electrochemical results were achieved for these samples. This indicated that the phase $\text{Nd}_{0.05}\text{Gd}_{0.15}\text{Ce}_{0.80}\text{O}_{2-\delta}$ had suitable properties to be considered for future work.

Fig. 2. XRD pattern for NGCO-LSCF cathode materials (a) at room temperature, and (b) after treatment at 1100 °C for 4h under static air

Fig.3. SEM micrograph of symmetrical cell LSCF | CGO20 | LSCF cross section, showing LSCF as cathode material on left side and CGO as electrolyte material on right side

Fig. 4. SEM micrographs of the porous electrode surface of (a) LSCF, (b) LSCF-NGCO1, (c) LSCF-NGCO3, (d) LSCF-NGCO5, and (e) LSCF-NGCO7 sintered at 1100 °C for 4h.

3.3. Thermal analysis

A decrease in mass was observed for all the samples (Fig. 5), which corresponded to the creation of oxygen vacancies, thereby losing lattice oxygen [25-27]. Babu *et al.* also showed that the GCO doping with trivalent ions led to the generation of oxygen vacancies [8].

Fig.5. Thermo-gravimetric analysis performed on reduced powders. The samples were heated up under 5% H₂/Ar until 900 °C (for 4 h) using a ramp rate of 1 °C min⁻¹.

However, the mass loss increased for the composite samples with an increase in Nd content. This can be related to the charge compensation effect due to co-doped rare earth trivalent ions on Ce⁴⁺ sites in the composites. Moreover, the higher disordered oxygen vacancies and electronic conductivity may lead to overwhelming oxygen ion mobility [28, 29]. The defect concentration during the formation of NGCO can be explained by Kroger-Vink notation:

where, RE represents Gd^{3+} and Nd^{3+} rare-earth ions, RE' represents a Ce^{4+} site which is replaced with RE components, $\dot{V}_o$ is an oxygen vacancy with doubly positive charge, and O_o^x is a neutral oxygen at an oxygen site.

The oxygen non-stoichiometry (δ) is calculated from the mass loss during the TGA test when heated to 900 °C using following formula

$$\delta = \Delta m_s \cdot \frac{M_s}{M_o} \tag{3}$$

Where Δm_s is the mass loss measured in the sample, M_s is the molar mass of the stoichiometric oxides ($g\ mol^{-1}$) of the composite, and M_o is the molar mass ($g\ mol^{-1}$) of the oxygen in the sample.

The main extent of reduction for LSCF-based composites is taking place between 400 °C and 600 °C. Table 1 summarizes the oxygen non-stoichiometry calculated from TGA results for all the samples. Comparable behavior has also been reported for LSCF6428 by Papergyriou et al. in reducing environment (5% H_2/Ar) [25].

Table 1 Mass loss and corresponding oxygen non-stoichiometry of LSCF and composites

Sample	Mass loss (%)	Oxygen non-stoichiometry (δ) oxygen per unit formula
LSCF6428	0.93	0.135
LSCF-NGCO1	0.94	0.222
LSCF-NGCO3	0.95	0.223
LSCF-NGCO5	1.02	0.242
LSCF-NGCO7	1.05	0.249

3.4. Electrochemical impedance measurement

Fig. 6 shows the Nyquist plots of symmetrical cells under synthetic air at 800 °C. The figure compares both the use of the new proposed co-doped ceria oxide as an electrode material and the amount of Nd in the formula (1%, 3%, 5% and 7%).

Fig.6. Electrical impedance spectra of symmetrical cells characterized at 800 °C in an air flow rate of 150 sccm

Interestingly, the overall impedance arc size decreased with the increase for dopant (Nd). The electrode polarization resistance (R_p) was obtained directly from impedance spectra by subtracting the low frequency and high frequency intercepts on the real axis. The best results

were observed when the Nd concentration was 5%; R_p decreased considerably with respect to the symmetrical cell only with LSCF material and lower Nd/Ce ratio. As can be seen in the plot, upon further increase in the Nd content to 7%, the arc size increases drastically. This indicates there is a limit in the doping to achieve improvements in the electrochemical properties. The impedance spectroscopy analysis for the composite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{2-\delta}\text{-Nd}_{0.05}\text{Gd}_{0.15}\text{Ce}_{0.80}\text{O}_{2-\delta}$ (LSCF-NGCO5) showed better polarization resistances under higher thermal energy (Fig. 7).

Fig. 7. Electrical impedance spectra of LSCF-NGCO5 cathodes characterized in symmetrical cells in an air flow rate of 150 sccm at 650 °C, 700 °C, 750 °C and 800 °C.

The Arrhenius plot for area specific resistance (ASR) of different symmetrical cells versus

temperature are reported in Fig. 8. The ASR was calculated from the impedance data using equation 4

$$ASR = \frac{R}{2} \times area \quad (4)$$

where R and area are the polarization resistance and the surface of the electrode, respectively. In above equation, R is further divided by 2 because of the symmetrical cell configuration.

Fig. 8. ASR versus Temperature for LSCF-NGCO cathodes characterized in symmetrical cells in an air flow rate of 150 sccm.

The calculated values of the ASR decreased with increase in temperature. The lowest polarization value of the composite LSCF-Nd_{0.05}Gd_{0.15}Ce_{0.8-x}O_{2-δ} cathode was found to be 0.06 Ω.cm² at 800°C, which was 25% lower than the value reported by Xiuan Xi *et al.* for La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{2-δ}-Gd_{0.10}Ce_{0.90}O_{2-δ} [30]. The calculated area specific resistance values for La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{2-δ}-Nd_{0.05}Gd_{0.15}Ce_{0.80}O_{2-δ} were 0.17, 0.31 and 0.59 Ω.cm² at 750, 700 and 650°C, respectively. These R_p were in close agreement with the values reported in literature for high performance composite cathodes [31, 32]. This can be attributed to the porous microstructure, causing an expansion of the available TPB length as well as increasing mobile oxygen vacancies, thus enhancing the ORR activity. However, when the content of co-dopant in the ceria electrolyte was further increased in the composite electrode material, i.e. above 5 wt. %, the cathode polarization resistance increased. It was reported previously that oxygen vacancies with smaller radii were formed if the increase in concentration of rare-earth dopants in ceria was above 20 wt.% [28]. This may prevent the oxygen ion movement through the sample due to producing longer conducting pathways in form of clustered oxygen vacancies, thereby increasing the polarization resistance [33, 34].

4. Conclusions

Single phase cubic fluorite structures based on the formula Nd_xGd_{0.15}Ce_{0.85-x}O_{2-δ} for x= 0.01, 0.03, 0.05 and 0.07 were synthesized successfully. Stability with the common SOFC cathode material LSCF was shown at high temperature under oxidizing atmospheres. By impedance spectroscopy, the effect of Nd content on polarization resistance was addressed. By increasing the

Nd co-dopant in the GCO matrix in the NCGO-LSCF composite, any further increase in Nd weight percentage in the composite meant lower polarization resistance. There was an unknown limit in the doping beyond 5%; as the R_p for $\text{Nd}_{0.07}\text{Gd}_{0.15}\text{Ce}_{0.78}\text{O}_{2-\delta}$ increased drastically.

Finally, findings of this study showed that 5% Nd co-doped GCO in an LSCF-NGCO composite qualified as a potential candidate as cathode material for future IT-SOFC applications. In addition, SEM micrographs showed that the electrode microstructure could be optimized to achieve improvements in the polarization resistance values. To optimize the porosity and to reduce the thickness of the electrodes, either screen printing or tape casting techniques should be employed in future work.

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