

Electrochemical performance of $\text{La}_2\text{NiO}_{4+\delta}\text{-Ce}_{0.55}\text{La}_{0.45}\text{O}_{2-\delta}$ as a promising bifunctional oxygen electrode for reversible solid oxide cells

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Abstract

In this work, $\text{La}_2\text{NiO}_{4+\delta}\text{-xCe}_{0.55}\text{La}_{0.45}\text{O}_{2-\delta}$ (denoted as LNO-xLDC) with various LDC contents ($x = 0, 10, 20, 30$ and 40 , wt %) were prepared and evaluated as bifunctional oxygen electrodes for reversible solid oxide cells (RSOCs). Compared with the pure LNO, the optimum composition of LNO-30LDC exhibited the lowest polarization resistance (R_p) of 0.53 and $0.12 \Omega\cdot\text{cm}^2$ in air at 650 and 750 °C, respectively. The enhanced electrochemical performance of LNO-30LDC oxygen electrode was mainly attributed to the extended triple phase boundary and more oxygen ionic transfer channels. The hydrogen electrode supported single cell with LNO-30LDC oxygen electrode displayed peak power densities of $276, 401$ and $521 \text{ mW}\cdot\text{cm}^{-2}$ at $700, 750$ and 800 °C, respectively. Moreover, the electrolysis current

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density of the single cell demonstrated $526.39 \text{ mA}\cdot\text{cm}^{-2}$ under 1.5 V at 800 °C, and the corresponding hydrogen production rate was $220.03 \text{ ml}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$. The encouraging results indicated that LNO-30LDC was a promising bifunctional oxygen electrode material for RSOCs.

Keywords: $\text{La}_2\text{NiO}_{4+\delta}$; oxygen electrode; electrochemical performance; reversible solid oxide cells

1 Introduction

Reversible solid oxide cells (RSOCs) are promising energy storage and regeneration devices, which have attracted worldwide attention due to its multi-function, high energy, low pollution and so on [1,2]. RSOCs are capable of operation in the solid oxide fuel cell (SOFC mode) for electricity generation from fuel as well as the solid oxide electrolysis cell (SOEC mode) for hydrogen generation from electrolysis of steam [3,4]. However, the polarization loss of the bifunctional oxygen electrode is the key factor limiting the overall performance of RSOCs, which mainly dominated by its electrocatalytic activities for both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [5,6]. Considerable efforts have been devoted to reduce the polarization loss of the oxygen electrode by exploring novel materials [7,8]. However, oxygen electrode materials with satisfactory electrochemical performances for RSOCs are still elusive.

Alternatively, $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) as the mixed ionic and electronic conductor (MIEC) material with the K_2NiF_4 -type structure has been regarded as a promising candidate oxygen electrode material due to its moderate thermal expansion coefficient ($\sim 13.0 \times 10^{-6} \text{ K}^{-1}$), high oxygen ion conductivity ($\sim 0.02 \text{ S}\cdot\text{cm}^{-1}$ at 700 °C) and

favorable electrochemical performance caused by the additional two phase boundary (2PB) [9-11]. The crystal structure of LNO consists of alternating stacked La_2O_3 rocksalt layers and LaNiO_3 perovskite layers along the c direction [12,13]. Moreover, in order to reduce the structural stress between the La-O and Ni-O bondings, excess oxygen (denoted as δ) can accommodate into La_2O_3 rocksalt layers, which lead to the high ionic conductivity due to the migration of interstitial oxygen in rocksalt layers [14-16]. The electrochemical performance of LNO oxygen electrode has been investigated on SDC substrates, which demonstrated a low polarization resistance of $0.38 \text{ } \Omega \cdot \text{cm}^2$ at $800 \text{ } ^\circ\text{C}$ [17]. In addition, LNO oxygen electrodes with thickness varying from 5 to 30 μm were also evaluated and confirmed the electrocatalytic properties of LNO electrode with a thickness of about 20 μm achieved the lowest polarization resistance ($0.24 \text{ } \Omega \cdot \text{cm}^2$ at $800 \text{ } ^\circ\text{C}$) [18]. In contrast, the influence of microstructure on electrochemical performance of LNO electrode was also evaluated and indicated the role of surface diffusion of oxygen [19,20]. Furthermore, adding various electrolyte compositions (such as $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC), $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_{1.96}$ (YSZ) and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) to form composite oxygen electrode is a common way to further improve the electrode/electrolyte/gas triple phase boundary (3PB) [21,22]. Hence, composite oxygen electrode prepared by LNO infiltration into porous electrolyte backbone or physically mixing the pristine materials exhibited improved performance. Although the LNO itself was thermodynamically stable, the possible solid state interaction between various components in LNO-based composite electrodes may occur at high temperature [23]. Decomposition of LNO in LNO-SDC composites was

observed after sintering at 1300 °C for 5 h, which lead to the formation of Sm, La co-doped ceria $\text{Sm}_{0.2}\text{La}_{0.23}\text{Ce}_{0.57}\text{O}_{2-\delta}$ [24]. Furthermore, a thermodynamics-based design for $\text{LNO}:\text{La}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ composite indicated the improved phase stability [25].

In this work, a series of $\text{La}_2\text{NiO}_{4+\delta-x}\text{La}_{0.45}\text{Ce}_{0.55}\text{O}_{2-\delta}$ (denoted as LNO-xLDC) were prepared by mixing LNO and LDC in various weight ratios. The electrochemical properties of LNO-xLDC oxygen electrodes were systematically investigated in detail to determine the optimal LDC content in the composite. The effects of LDC addition on the microstructures and electrochemical performances of oxygen electrodes were also discussed. Furthermore, the electrochemical properties of the hydrogen electrode supported single cell with the LNO-30LDC oxygen electrode was investigated both in the SOFC mode and SOEC mode at 700-800 °C.

2 Experimental

2.1 Preparation of powders

All of the starting chemicals were analytical grade, which was used directly without any further purification. $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) powders were synthesized by the sol-gel method. All metal nitrates in the requisite stoichiometric ratio were dissolved in distilled water, followed by the introduction of citrate acid as the complexing agent at a molar ratio of 1:1.5 for the total metal ions and citrate acid. The solution was heated at 80 °C for 4 h under stirring and then dried at 200 °C for 12 h in order to remove residual water. Subsequently, the dry gel was successively pre-calcined at 800 °C for 4 h, ground for 1 h and then calcined at 1100 °C for 4 h in air to obtain the final black LNO powders. $\text{Ce}_{0.55}\text{La}_{0.45}\text{O}_{2-\delta}$ (LDC) and $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) powders were also

prepared by the same procedure as mentioned above, respectively. The final calcination condition of LDC and SDC powders was 800 °C for 4 h. The composite samples were prepared by adding LDC powders in the amount of 10, 20, 30 and 40 wt.% to LNO powders (LNO-xLDC). The mixtures were ground using a mortar for 2 h to ensure uniform distribution.

2.2 Fabrication of symmetric cells and single cells

The electrochemical performance was evaluated based on symmetrical cells with a LNO-xLDC|SDC|LNO-xLDC configuration. The SDC substrates for symmetrical cells were prepared with SDC powders via dry pressing uniaxially at 300 MPa for 1 min and then sintering at 1400 °C for 4 h. The thickness of dense SDC disks was about 350 μm. The slurry for each composite electrode was prepared by mixing electrode materials with terpineol solution of 7 wt.% ethylic cellulose in a weight ratio of 7:3. Subsequently, the slurry was symmetrically coated on both sides of SDC disks, and then sintering at 1100 °C for 4 h in air to obtain the symmetrical cell. The area of the oxygen electrode was 0.12 cm². Moreover, the silver paste (DAD-87, Shanghai Research Institute of Synthetic Resins, China) was coated on surface of the oxygen electrode as current collector.

The hydrogen electrode supported single cell (NiO-YSZ|YSZ|SDC|LNO-30LDC) was fabricated by the similar procedure as previously described [26]. Briefly, NiO and YSZ powders with a weight ratio of 5:5 were mixed uniform and pressed uniaxially at 300 MPa. NiO-YSZ disks were pre-sintered at 1000 °C for 2 h. Subsequently, the YSZ electrolyte layer was applied onto NiO-YSZ disks using the slurry spin coating

method, which were sintered at 1400 °C for 4 h. The SDC barrier layer was also coated on the surface of the YSZ layer to prevent the detrimental interaction. Finally, the LNO-30LDC slurry was painted on hydrogen electrode supported half cells and sintered at 1100 °C for 4 h to form the porous oxygen electrode layer.

2.3 Characterization on microstructure and electrochemical performance

Phase compositions of LNO-30LDC was examined by X-ray diffraction (XRD, Rigaku D/max2200, Japan). The surface and cross-section microstructure of oxygen electrodes were observed by a field emission scanning electron microscope (SEM, HitachiSU800, Japan). Energy-dispersive X-ray spectroscopy analysis was applied to observe the distribution of various elements across the interface between the oxygen electrode and electrolyte.

The electrochemical impedance spectra (EIS) measurements of symmetric cells with LNO-xLDC were obtained under open-circuit voltage over the frequency range from 10 mHz to 100 kHz with the AC signal amplitude of 10 mV. Moreover, the hydrogen electrode supported single cell using LNO-30LDC as the oxygen electrode was tested at the temperature range from 700 to 800 °C (50 °C intervals). The single cell was sealed on the top of an alumina tube. For power generation (SOFC mode), dry hydrogen at the flow rate of 50 ml·min⁻¹ was fed to the hydrogen electrode, while the oxygen electrode was exposed to stationary air. Furthermore, for steam electrolysis (SOEC mode), steam with hydrogen carrier gas at a rate of 100 ml·min⁻¹ was fed to the hydrogen electrode. The absolute humidity (AH, the vol.% of humidity in the total gas volume) of the mixture gas was about 30 vol.%. Hydrogen generation

rate of steam electrolysis was calculated from the Faraday's law, assuming 100% current efficiency [27,28]. The current-voltage curves (I-V) and EIS data of the single cell were collected by an electrochemical workstation (Bio-logic VSP, France).

3 Result and discussion

The XRD pattern of LNO-30LDC powders after calcined at 1100 °C for 4 h was presented in Fig. 1. It clearly indicated that all peaks of LNO-30LDC can be identified with a physical mixture of LNO and LDC. No additional peaks were observed. The structures of LNO and LDC in LNO-LDC after sintered at 1100 °C for 4 h remained unchanged, which revealed no obvious chemical reaction occurs. Hence, the result confirmed the chemical compatibility between LNO and LDC, which is consistent with the previous report [25].

The surface morphology of various composite oxygen electrodes was observed as shown in Fig. 2. The typical morphology as shown in Fig. 2c displayed that LNO surface was surrounded by the finer LDC particles. Similar phenomena have also been reported in other composite systems, such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -SDC [29]. Clearly, the grain size of LNO was about 2 μm , while LDC had a smaller grain size (about 100-300 nm). Sufficient contact between LNO and LDC particles was beneficial to the expansion of 3PB areas and the formation of oxygen ion transport channels, which could facilitate their electrocatalytic activities [30].

Furthermore, the cross-section of the symmetrical cell with LNO-30LDC electrode was also observed (Fig. 3a). The LNO-30LDC electrode with a thickness of 22 μm was tightly bonded to the surface of the dense electrolyte without any cracks or

separation. Energy-dispersive X-ray spectroscopy linear scan analysis across the interface between LNO-30LDC oxygen electrode and SDC electrolyte was also measured as shown in Fig. 3b. Obviously, the content of La and Ni was decreased rapidly at the interface of SDC electrolyte and LNO-30LDC electrode, while the content of Ce increased sharply, which also indicated that there was no obvious elemental diffusion or detrimental solid state interaction.

The impedance spectra of the symmetric cell with LNO-xLDC oxygen electrodes were measured to evaluate the electrochemical performance of various oxygen electrodes. The high frequency intercept dominated by the ohmic resistance (R_{ohm}) was normalized to zero in Nyquist plots. Fig. 4a and 4b displayed the typical Nyquist plots of symmetrical cells with LNO-xLDC oxygen electrodes at temperature of 650 and 750 °C, respectively. The polarization resistance (R_p) of LNO-xLDC composite at 650 and 750 °C decreased with increasing x from 0 to 30 wt.% and then increased. Furthermore, the $LR_{\text{ohm}}(R_{\text{H}}CPE1)(R_{\text{L}}CPE2)$ equivalent circuits (Fig. 4a, b inset) were implemented to fit the impedance spectra. Here, L is the inductance and total polarization resistance is expressed as $R_p=R_{\text{H}}+R_{\text{L}}$. R_{H} and R_{L} were corresponded to the high and low frequency arcs, respectively. The high frequency arc (R_{H}) was related with the charge transfer process, while the low frequency arc (R_{L}) can ascribe to bulk or surface oxygen diffusion process and the oxygen dissociation [31]. Among the evaluated various compositions, LNO-30LDC electrode possessed the lowest R_p ($0.12 \Omega \cdot \text{cm}^2$ at 750 °C and $0.53 \Omega \cdot \text{cm}^2$ at 650 °C, respectively) as shown in Fig. 4c, which also were lower than the literature data in Table 1. It should be note that the R_p at 750

°C of LNO-30LDC oxygen electrode was even comparable with the LNO infiltrated YSZ electrode, which mainly contributed to the effective connection between LNO and LDC particles as well as the expansion of 3PB [30,32]. The Arrhenius plots of the total R_p for LNO-xLDC composite cathodes displayed in Fig. 4d. LNO-30LDC oxygen electrode revealed the activation energy of $113.2 \text{ kJ}\cdot\text{mol}^{-1}$, which was relatively lower than that of LNO cathode ($118.9 \text{ kJ}\cdot\text{mol}^{-1}$) in this work as well as the $121.9 \text{ kJ}\cdot\text{mol}^{-1}$ of LNO cathode reported previously [38].

To further explain the mechanism of oxygen reduction reaction, the possible sub-steps of oxygen reduction reaction in LNO and LNO-xLDC oxygen electrode on SDC electrolyte were schematically illustrated in Fig. 5. The overall oxygen reduction reaction on the oxygen electrode can be described as $\frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^- = \text{O}^{2-}$, which contains several sub-steps, such as the gaseous oxygen adsorption-dissociation on the oxygen electrode surface ($\text{O}_2(\text{g}) \rightleftharpoons \text{O}_{2,\text{ads}}$ and $\text{O}_{2,\text{ads}} \rightleftharpoons 2\text{O}_{\text{ads}}$), the charge transfer process ($\text{O}_{\text{ads}} + 2\text{e}^- + \text{V}_\text{O}^{\bullet\bullet} \rightleftharpoons \text{O}_\text{O}^\times$) as well as the ionic oxygen transfer process ($\text{O}_{3\text{PB}}^{2-} + \text{V}_\text{O}^{\bullet\bullet} \rightleftharpoons \text{O}_\text{O}^\times$) [39]. For the pure LNO oxygen electrode (Fig. 5a), the total oxygen electrode surface could be applied as active sites for oxygen reduction reaction, which signified the active region extends from the interface of the oxygen electrode and electrolyte to the entire oxygen electrode surface [40]. The electrochemical reactions of the oxygen electrode in the SOEC mode are the inverse to sub-steps in the SOFC mode. Hence, the expansion of the active region also contributes to the enhanced electrochemical performance of the oxygen electrode in SOEC mode [26].

Moreover, the addition of LDC with proper content in LNO not only provided more

oxygen ionic transfer channels but also formed more 3PB due to the extensive contact between LNO and LDC particles as shown in Fig. 5b, which played a vital role in the enhanced electrochemical performance of LNO-30LDC (Fig. 5c) [17]. However, the electronic transfer channels could not be effectively built up for LNO-40LDC with the addition of excess LDC, which lead to the sharp increase of R_p . Simultaneously, discontinuous electronic transport channels also resulted in the high ohmic resistance of composite oxygen electrode [41].

Furthermore, the electrochemical performance of LNO-30LDC oxygen electrode was also evaluated using the hydrogen electrode supported single cell (NiO-YSZ|YSZ|SDC|LNO-30LDC). Fig. 6 presented the I-V curves and corresponding I-P curves of the single cell in the SOFC mode with dry H_2 as the fuel at 700-800 °C. The open circuit voltage was 1.05 V at 700 °C, revealing the well-sealed single cell. The maximum power densities of the single cell achieved 276, 401 and 521 $mW \cdot cm^{-2}$ at 700, 750 and 800 °C, respectively. Moreover, Fig. 7a displayed the impedance spectra of single cell with LNO-30LDC oxygen electrode at various temperatures. R_p was decreased with the increase of operation temperature due to the higher electrocatalytic activity of LNO-30LDC oxygen electrode at the elevated temperature. As can be observed in Fig. 7(b), the intermediate to low frequency range features the dominating process [42]. Moreover, the Bode plot peaks shift towards low frequencies with increasing temperature, which mainly corresponds to impedances related to diffusion or mass transport processes [43]. Hence, LNO-30LDC oxygen electrode displayed encouraging performance in the SOFC

mode.

In order to evaluate the overall performance of the LNO-30LDC oxygen electrode in RSOCs operation, the hydrogen electrode supported single cell was measured at 700-800 °C under both in the SOFC mode and the SOEC mode. When the open circuit voltage was higher than the applied voltage, the cell operated in the SOFC mode and generated electricity with the consumption of fuel. By contrast, when the open circuit voltage was lower than the applied voltage, the cell operated in the SOEC mode and splits H₂O into H₂ and O₂ with the consumption of electricity [44]. As shown in Fig. 8a, the the open circuit voltage values of the single cell were around 1.01 V, which indicated the cell was well sealed. The slope of I-V curves increased with operation temperature increasing from 700 to 800 °C. Moreover, the electrolysis current density was increasing with the increasing of applied electrolysis voltage from the open circuit voltage to 1.5 V. The current densities achieved 270.86, 445.06 and 526.39 mA·cm⁻² at 700, 750 and 800 °C under applied electrolysis voltage of 1.5 V, respectively. To further reveal the hydrogen generation properties of the single cell with LNO-30LDC oxygen electrode, hydrogen production rates can be directly calculated according the measured current data as Eq. (1) [27]:

$$\Delta N_{H_2} = \frac{-I}{2F} \quad (1)$$

The molar rate of hydrogen generation is expressed as ΔN_{H_2} . I and F is the electrical current and the Faraday's constant, respectively. Hydrogen production rates was 113.22, 186.03 and 220.03 mL·cm⁻²·h⁻¹ at 700, 750 and 800 °C under 1.5 V, respectively. All above very promising results revealed that LNO-30LDC was a good

candidate as the oxygen electrode for RSOCs.

4 Conclusions

In summary, a series of $\text{La}_2\text{NiO}_{4+\delta-x}\text{Ce}_{0.55}\text{La}_{0.45}\text{O}_{2-\delta}$ composites (LNO-xLDC) with various LDC contents ($x = 0-40$, wt.%) were investigated as oxygen electrodes for RSOCs. The XRD results revealed no other by-product phases occurred in LNO-30LDC after sintering at $1100\text{ }^\circ\text{C}$ for 4 h. Proper adding of LDC in LNO-xLDC revealed improved electrochemical performance than that of pristine LNO, which was mainly attributed to the expansion of 3PB and more oxygen ionic transfer channels. LNO-30LDC oxygen electrode displayed the lowest R_p value ($0.12\ \Omega\cdot\text{cm}^2$) at $750\text{ }^\circ\text{C}$. Furthermore, the maximum power density of hydrogen electrode supported single cell with LNO-30LDC oxygen electrode achieved $521\ \text{mW}\cdot\text{cm}^{-2}$ at $800\text{ }^\circ\text{C}$. The electrolysis current density of the single cell demonstrated $526.39\ \text{mA}\cdot\text{cm}^{-2}$ under 1.5 V at $800\text{ }^\circ\text{C}$, and the corresponding hydrogen production rate was $220.03\ \text{ml}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$. All above results suggested that LNO-30LDC was a promising bifunctional oxygen electrode material for RSOCs.

Acknowledgments

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