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Investigations on electrochemical performance of La$_2$NiO$_4$$_{+\delta}$ cathode material doped at A site for solid oxide fuel cells

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Abstract

In this work, the perovskite compounds La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba), which is one kind of mixed ionic electronic conductors (MIEC) with perovskite structure, was explored as cathode materials for proton conducting solid oxide fuel cells (H-SOFCs). In order to understand how the size of A-site cations affects material properties, the electrical conductivity and the electrochemical performances of La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) were compared. The results are more interesting. In the middle temperature region (600 °C–700 °C), Ca doping is the best choice among the three alkaline earth elements. In the low temperature region (300 °C–600 °C), Sr-doped single cells Sr-doped single cells have better performance. However, Ba doping easily generates BaCO$_3$ impurities, which reduces the ion transmission capacity and increases the interface resistance, resulting in poor performance of the single cell. This work shows that La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca and Sr) is the main cathode candidate material for H-SOFC.

1. Introduction

In today’s era, with the development of science and technology and the improvement of human living standards, human demand for energy will increase substantially. The excessive consumption of limited terrestrial hydrocarbon natural resources will cause global warming, environmental pollution and energy shortage [1]. SOFCs are electrochemical energy conversion devices which can convert chemical energy stored in fuel into electrical energy directly for our use [2]. They have high energy efficiency, low pollution as well as good fuel flexibility. It can use a variety of types of clean energy to provide a viable solution for energy shortages and environmental pollution [3]. At present, the focus of SOFC research is to lower the operating of SOFCs temperature to meet the goal of reducing costs and improving durability [4]. In order to improve the cathode reaction rate, the MIEC cathode materials have always been a research hotspot [5]. These functional materials allow ions (usually oxygen ions, O$^{2-}$) and electrons to be conducted simultaneously, and are a composite element of an electronic conductive phase and an oxygen ion conductor [6, 7].

La$_2$NiO$_4$ oxides, which possess layered Ruddlesden-Popper (R-P) structure are promising materials for such SOFCs applications for their high oxygen mobility [8, 9]. Although La$_2$NiO$_{4+\delta}$ material has proton blocking properties, R-P material is still considered as a potential cathode material H-SOFC [10, 11]. Some MIEC materials with perovskite structure have been explored extensively, such as Sm$_{0.2}$Sr$_{0.8}$Co$_{2–\delta}$ [12], Ba$_{0.6}$Sr$_0.4$Co$_{0.8}$Fe$_{0.2}$O$_{3–\delta}$ [13] and La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3–\delta}$ [14] and La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3–\delta}$ [15] or LnBaCo$_{2+\delta}$ (Ln = Pr, Nd, Sm, Gd, Y) [6, 16]. High-performance single cells based on La$_2$NiO$_{4+\delta}$ cathode have been demonstrated (the power density is larger than 500 m W · cm$^{-2}$ at 700 °C). La$_2$NiO$_{4+\delta}$ exhibit the advantages of high oxygen permeation coefficients ($D = 2 \times 10^{-7}$ cm$^2$ s$^{-1}$) and surface exchange coefficients.
(k = $2 \times 10^{-6}$ cm s$^{-1}$)\cite{17}. They have relatively high electron and ion conductivity and a coefficient of thermal expansion (TEC) compatible with common electrolytes\cite{18}. It has been reported that doping other ions at the A or B position of La$_2$NiO$_4$ can reduce strain and affect physical and chemical properties\cite{19}. Alkaline earth elements Ca, Sr or Ba are suitable A site dopants for La$_2$NiO$_4$\cite{20, 21}. Since there are hyperstoichiometric oxygen in tetrahedron of La$_2$NiO$_4$ materials, the oxygen ions at gap sites can facilitate the oxygen ions transfer. Not only that, La$_2$NiO$_4$ materials exhibit high electronic conductivity for the mixed valences of B-site metal ions, and have good catalytic activity in oxygen reduction reaction.

So far, research has focused on the La$_2$-Sr$_x$NiO$_4$ system\cite{22}. Related studies on Ca and Ba doped La$_2$NiO$_4$ have rarely been reported. Since Ca, Sr or Ba have different ionic radius doping them into A-site will cause different distortions of lattice, resulting in different electrochemical properties. Therefore, we studied the effects of ionic radius of different A-site dopants on the cathode performance of La$_2$NiO$_4$ and study the internal mechanism. In our work, the widely used BaZr$_{0.1}$Ce$_{0.2}$Y$_{0.7}$O$_{3-\delta}$ (BZCY) was used as the electrolyte of H-SOFCs. The La$_{1.5}$A$_{0.5}$NiO$_{4-\delta}$ (A = Ca, Sr or Ba) cathodes were prepared to study their electronic conductivity and electrochemical performance\cite{23}.

2. Experimental

2.1. Powder synthesis

NiO-BZCY, BaZr$_{0.1}$Ce$_{0.2}$Y$_{0.7}$O$_{3-\delta}$ (BZCY), La$_{1.5}$A$_{0.5}$NiO$_{4-\delta}$ (A = Ca, Sr or Ba) and other key components of the powder material were synthesized by citric acid-nitrate combustion method. Taking the electrolyte powder material BZCY as an example, the detailed steps of the synthesis are as follows. First, BaCO$_3$ (99.9%, 3 N, Sinopharm Chemical Reagent Co., Ltd, hereinafter referred to as SCR) and Zr(NO$_3$)$_2$·5H$_2$O and Y(NO$_3$)$_2$·6H$_2$O (99.9%, 3 N, SCR) dissolved in dilute HNO$_3$ in stoichiometric ratio, after stirring and dissolved, add Ce(NO$_3$)$_3$·6H$_2$O (analytical grade, $\geq 99.0\%$, SCR) in stoichiometric ratio; then, add metal ion molar ratio 1.5 times citric acid complexation, using ammonia water to increase the pH of the solution to 7. After the complexation is fully completed, the solution is transferred to an electric furnace for heating. As the solution moisture evaporates, the solvent gradually transforms to a gel, and the heating is continued, and the wet gel transforms into a dry gel, thereby causing self-propagating combustion phenomenon and obtaining a primary. The precursor powder; finally, the precursor powder was sintered at 1050 °C for 3 h to form pure BZCY.

2.2. Cell fabrication

The anode composite powders consist of NiO and BZCY in weight ratio of 6:4. We use 20 wt.% starch as the pore former to achieve high porosity in NiO-BZCY after sintering. The half cells with the structure of NiO-BZCY | BZCY were fabricated by dry-pressing method. The green half-cells were co-sintered at 1400 °C for 5 h \cite{24}. The cathode La$_{1.5}$A$_{0.5}$NiO$_{4-\delta}$ (A = Ca, Sr or Ba) powders were grinded thoroughly with the 6% ethylcellulose-terpineol binder to form cathode slurry. Then the cathode slurry was painted on the surface of electrolyte membrane and co-fired at 1000 °C for 3 h, then we can obtain the final single cells. The silver paste, which serves as current collectors, should be painted on the surface of cathode for all single cells in this study\cite{24}.

2.3. Characterization

We use x-ray diffractometer (XRD, Rigaku TTR-III) with CuKα radiation to characterize the phase of the synthesized powders. Scanning electron microscopy (SEM, JEOL JSM-6700F) was used to observe the microstructure and morphology of cellular components. In order to measure the conductivity of La$_{1.5}$A$_{0.5}$NiO$_{4-\delta}$ (A = Ca, Sr or Ba), a dense La$_{1.5}$A$_{0.5}$NiO$_{4-\delta}$ (A = Ca, Sr or Ba) cathode rod was fabricated. We use four-probe DC method to test the electrical conductivity from 200 °C–800 °C in air\cite{24}.

2.4. Electrochemical measurement

The NiO-BZCY | BZCY cathode single layer battery was tested under the same conditions in a self-made battery test system between 550 °C and 700 °C. Humidified hydrogen (~3% H$_2$O) at a flow rate of about 30 ml min$^{-1}$ was used as fuel gas while ambient air was used as fuel and oxidant, respectively. The I-V curves were collected using a DC Electronic Load (ITech Electronics model IT8511) based on a two-probe configuration. The Electrochemical impedance spectroscopy was measured under open circuit conditions using an impedance analyzer (CHI604E, Shanghai Chenhua)\cite{23}. The AC signal voltage is 5mV and the frequency is scanned from 100 kHz to 0.1 Hz. The ohmic resistance and polarization resistance data of the single-cells were analyzed from the impedance spectrum\cite{23}.
3. Results and discussion

3.1. XRD analysis

Figure 1(a) shows the XRD pattern of La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) powder calcined at 1000 °C for 3 h (PDF 05-0378), a heterogeneous phase of BaCO$_3$ (toxic heavy stone phase) occurs. This indicates that Ba$^{2+}$, which has a larger ionic radius, is twisted when doping into the A site, resulting in a BaCO$_3$ impurity phase. This is highly consistent with the results of the previously reported work by Yujun Zhu [25]. First, all samples were crystallized in a tetragonal structure I4/mmm space group, but La$_{1.5}$Ba$_{0.5}$NiO$_{4+\delta}$ has a heterogeneous BaCO$_3$ formation. The phase purity of the BCZY and NiO-BCZY powders were also examined. The results showed that there are no impurity phases in both BCZY and NiO-BCZY (figure 1(b)) [24].

3.2. Electrical conductivity

Figure 2 shows the electrical conductivity of La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) measured by the four-probe DC method. Since the ionic conductivity is very low, so that we can neglect the ionic conductivity. The total conductivity can be considered as the electronic conductivity [19]. The conductivity of the sample of La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ reaches the
maximum conductivity in the range of 300 °C–400 °C, and La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca and Ba) reach the maximum conductivity in the range of 600 °C–800 °C. And under isothermal conditions and the same dopant level, the conductivity of La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ is much higher than that of La$_{1.5}$Ba$_{0.5}$NiO$_{4+\delta}$ and the conductivity of La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$. This can be explained by the change in the concentration and mobility of electron holes. The replacement of La by aliovalent element A can cause the electron holes generation in nickel site or the decrease of oxygen in lattice. The following equations (1) and (2) can help us understand [19], respectively.

$$
AO + Ni_{Ni}^{2+} \xrightarrow{La_{Ni}O_{4}} A_{La}^{+} + Ni_{Ni}^{2+} + O_{2}^{-}
$$

$$
2AO + O_{2} \xrightarrow{La_{Ni}O_{4}} 2A_{La}^{+} + 2O_{2}^{+} + \frac{1}{2}O_{2}(g)
$$

The former reaction triggers the oxidation of partial Ni$^{2+}$ to Ni$^{3+}$ and increases the number of charge carriers since these materials are p-type conductors, while the latter reaction makes oxygen content of materials less [19]. These two reactions occur simultaneously and they have competitive relationship. In figure 2, the increased conductivity indicates that the former is the primary charge compensation mechanism. Substituting La with a larger Sr atom can improve the stability of the La$_{2}$NiO$_{4+\delta}$ structure and increase the electron conductivity as the Ni-O$_{2}$ bond length is shortened.

### 3.3. SEM analysis

Figure 3 shows the SEM images of single cell with three layers of NiO-BZCY (anode) | BZCY(electrolyte) | La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba, anode), which has undergone heating and cooling processes during the electrochemical tests between 550 °C–700 °C. From figure 3(a), it can be observed that the electrodes adhere tightly to the electrolyte surface without obvious breakage or shedding, which indicates that the cathode and BZCY have good thermal compatibility. The strong adhesion of the cathode layer to the electrolyte is important because it results in less contact resistance and promotes charge transfer rate at the interface of cathode and electrolyte. Figure 3(a) shows that the electrolyte after sintering at 1350 °C is dense, which can avoid the leakage of reducing gas and allows the proton transport. The thickness of the electrolyte can be controlled substantially between 18–23 μm. Due to the nearly identical thick electrolyte and good compatibility between cathode and electrolyte, different cell performance should be related to the inherent characteristics of the different cathodes. Figures 3(b)–(d) are La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) magnified SEM images of the cathode microstructure. It can be seen that the cathode has porous morphology. The highly porous micro-structure will facilitate the rapid diffusion of gas oxygen into the cathode and reduce the loss of mass transfer polarization. In figures 3(b)–(d) that when the sintering temperature is the same, as the doping ion radius increases, the material particle size increases slightly. The specific surface area increases while particle size decreases, which results in active sites. La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ cathode particles are smallest, so that La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ cathode is supposed to have good performance.
3.4. Electrochemical performance

To evaluate the electrochemical performance of La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) materials for IT-SOFCs [26]. Since all single cells are fabricated in the same method and have nearly the same thickness of BZCY electrolyte [26], it can be considered that the difference in cell performance is caused by the different cathodes we used. The I-V and I-P curves for individual cells with different cathodes (La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr and Ba)) at 700 °C are plotted in figure 4(a). The maximum power density (MPD) of La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$, La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ and La$_{1.5}$Ba$_{0.5}$NiO$_{4+\delta}$ as the cathode of the cathode at 700 °C is 877,656,513 mW·cm$^{-2}$, respectively. As shown, the current density of the cell with La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ cathode is largest, which will result in the highest MPD value. The highest power output of the single cells using La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ as the cathode at 550 °C, 600 °C, 650 °C and 700 °C are 162, 313, 631 and 877 mW·cm$^{-2}$, respectively in figure 4(b). The power density (MPD) of different single cells having a La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) cathode is shown in table 1. The highest power output of La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ as the cathode indicates that La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ has the best electrochemical properties and conforms the impedance measurement results discussed later.

Figure 3. (a) Cross-sectional morphology of single cells SEM images (b), (c) and (d) are SEM images of cross-sectional morphology of La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) cathodes, respectively.

Figure 4. (a) I-V and I-P curves of a single cell NiO-BZCY|BZCY|La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) supported by anode at 700 °C and (b) I-V and I-P curves of different temperatures of La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ cathode.
A typical electrochemical impedance spectroscopy (EIS) of the cathode La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ at 550 °C–700 °C was shown in figure 5. The high frequency intercept with real axis represents the ohmic resistance (R$_o$), including the ionic resistance of the electrolyte, the resistance of the electrode, and contact resistance from the interface of the component. The low frequency intercept represents the total resistance (R$_t$) [27], which contains R$_o$ and polarization resistance (R$_p$). Other cathodes have similar trends in EIS at 550 °C–700 °C, so they are not placed here. The Ro and Rp of different single cells in the range of 550 °C–700 °C are shown in table 2. All resistance values decrease with increasing higher temperature, indicating that the corresponding electrochemical reaction is a thermal activation process [27]. In the case of a cell with La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ as a cathode, as the test temperature increases from 550 °C to 700 °C, the Rp value is reduced from 1.035 to 0.061 Ω cm$^2$. Under the same conditions, the value of Ro decreased from 0.375 to 0.199 Ω cm$^2$. We can conclude that the cell Rp controls the downward trend of Rt and plays a major role in total resistance decrease below 600 °C. Therefore, the key points of exploring better cathodes is to reduce Rp and enhance cell performances in lower temperature, so that we can reduce the operation temperature of SOFCs. Among three cathodes [27], La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ has the lowest Rp at 700 °C, 650 °C, 600 °C and 550 °C, which are 0.061, 0.206, 0.472, 0.1442, respectively. The highest power output discussed is consistent.

In order to further analyze the electrochemical parameters, the data in table 1 is plotted as a histogram (figure 6). An interesting phenomenon was found. The performance of single cells with La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ and La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ cathodes in the middle temperature range (600 °C–700 °C) is contrary to their electrical conductivity. The single cell tested by La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ cathode in the temperature range of 700 °C shows the best performance, which may be caused by the following reasons. First, as shown in figure 2, although the conductivity of La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ is much higher than that of La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (Ca and Ba), the difference in conductivity at 700 °C is not very large. Secondly, it may be the effect of the particle size of the material. As shown in figures 3(b)–(d), as the doping ion radius increases, the particle size of the material increases slightly, and the particle size of La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ is more smaller. When the unit cells are prepared at a certain temperature, the sintering properties of the perovskite materials determine their particle size. Smaller particle size can result in

| Table 1. The maximum power density of La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) at 550 °C, 600 °C, 650 °C, 700 °C, respectively. |
|--------------|--------|--------|--------|--------|
| Temperature  | 700 °C | 650 °C | 600 °C | 550 °C |
| La$_{1.5}$Ca$_{0.5}$NiO$_{4+\delta}$ | 877    | 631    | 313    | 162    |
| La$_{1.5}$Sr$_{0.5}$NiO$_{4+\delta}$ | 656    | 436    | 344    | 205    |
| La$_{1.5}$Ba$_{0.5}$NiO$_{4+\delta}$ | 513    | 387    | 259    | 164    |

| Table 2. The R$_o$ and R$_p$ values of a unit cell having La$_{1.5}$A$_{0.5}$NiO$_{4+\delta}$ (A = Ca, Sr or Ba) as a cathode were measured at 550 to 700 °C. |
|----------|--------|--------|--------|--------|--------|--------|--------|
| Temperature  | 700 °C | 650 °C | 600 °C | 550 °C |
| R$_o$  | R$_p$  | R$_o$  | R$_p$  | R$_o$  | R$_p$  | R$_o$  | R$_p$  |
| LCNO  | 0.199  | 0.061  | 0.233  | 0.149  | 0.289  | 0.382  | 0.374  | 1.035  |
| LSNO  | 0.220  | 0.128  | 0.252  | 0.254  | 0.348  | 0.545  | 0.472  | 1.305  |
| LBNO  | 0.253  | 0.127  | 0.333  | 0.232  | 0.428  | 0.560  | 0.607  | 1.442  |
higher specific surface area and more catalytic active sites [28]. Finally, there may also be the effects of Cr-poisoning and Sr-segregation mentioned by Simner [29], Alexander Beez et al [30]. It is the combined effect of these complex mechanisms that the La_{1.5}Ca_{0.5}NiO_{4+δ} cathode has more excellent battery performance than the La_{1.5}Sr_{0.5}NiO_{4+δ} cathode.

The single cell with La_{1.5}Ba_{0.5}NiO_{4+δ} as the cathode showed the worst overall performance. This phenomenon may be triggered by the BaCO_3 impurity phase in the La_{1.5}Ba_{0.5}NiO_{4+δ} cathode itself, which is proved by the XRD results shown in figure 1(a). The BaCO_3 is an insulator with very low oxygen ion or proton conduction. This impurity phase reduces the total ion transport capacity in cathode and increases the interface resistance. Therefore, it is similar to the pure phase cathode (La_{1.5}Ca_{0.5}NiO_{4+δ} and La_{1.5}Sr_{0.5}NiO_{4+δ}) single cells, single cells containing BaCO_3 impurity phase (La_{1.5}Ba_{0.5}NiO_{4+δ}) will result in lower cell performance.

As the temperature decreases, when the operating temperature reaches below 600 °C, the performance law of all single cells is consistent with the law of electrical conductivity. From figure 2, we can see that in the low temperature region (300 °C–600 °C), the conductivity of La_{1.5}Sr_{0.5}NiO_{4+δ} is much higher than that of La_{1.5}Ca_{0.5}NiO_{4+δ} and La_{1.5}Ba_{0.5}NiO_{4+δ}. This shows that the main factor affecting the electrochemical performance at this time is the conductivity characteristics of the materials themselves. Therefore, our electrochemical test results shows that La_{1.5}Ca_{0.5}NiO_{4+δ} performed best in the medium temperature range (600 °C–700 °C) La_{1.5}Ca_{0.5}NiO_{4+δ} and it is a potential cathode material for H-SOFCs. In the low temperature region (300 °C–600 °C), La_{1.5}Sr_{0.5}NiO_{4+δ} seems to be the more suitable cathode material.

4. Summary

In this work, La_{1.5}A_{0.5}NiO_{4+δ}(A = Ca, Sr or Ba) having a K_2NiF_4 type oxide has been studied as a cathode material for H-SOFCs in medium and low temperature range. All samples prepared with La_{1.5}A_{0.5}NiO_{4+δ}, (A = Ca, Sr or Ba) showed good compatibility with BZCY electrolyte after sintering. Ba doping easily produces BaCO_3 impurities and affects battery performance. Sr doping has the highest electronic conductivity. However, Ca doping exhibits the highest battery performance at high and intermediate temperature stages such as 700 °C, which may be a composite of factors such as the conductivity characteristics, particle size, Cr poisoning and Sr-segregation. In the low temperature region (300 °C–600 °C), the performance of La_{1.5}Sr_{0.5}NiO_{4+δ} cathode is better than La_{1.5}A_{0.5}NiO_{4+δ}(Ca and Ba). Therefore, Therefore, Ca-doped La_{2}NiO_{4+δ} can be considered as the cathode in the middle temperature region, and Sr-doped La_{2}NiO_{4+δ} impurity can be considered as the most promising cathode in the low temperature region. For the next work, optimizing the doping amount (x) of La_{2-x}A_{x}NiO_{4+δ}(A = Ca and Sr) provides a basis for further evaluation of the possibility of commercialization.

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Declaration of interest statement

We declare that we have no known competing financial interests or personal relationships that could may affect the work reported in this paper.

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