Pr$_{1.8}$La$_{0.2}$Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$O$_{4+\delta}$ as a potential cathode material with CO$_2$ resistance for intermediate temperature solid oxide fuel cell

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**Abstract**

Pr$_{1.8}$La$_{0.2}$Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$O$_{4+\delta}$ (PLNGC), a mixed ionic electron conductor (MIEC) with a K$_2$NiF$_4$-type structure, has been studied as a potential cathode material based on YSZ (ZrO$_2$ with 8 mol% Y$_2$O$_3$) electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs). The X-ray diffraction (XRD) analysis reveals that the good chemical compatibility between the PLNGC and YSZ. The maximum electric conductivity of the PLNGC appeared at about 460 °C and the value was 32 S cm$^{-1}$ in air and 34 S cm$^{-1}$ in O$_2$, respectively. A hollow fiber SOFC was fabricated with the PLNGC as the cathode, NiO–YSZ (1:1; w/w) as the anode and YSZ as the electrolyte. The maximum power density of the cell is 876 mW cm$^{-2}$ and the corresponding polarization resistance of the cell is 0.41Ω cm$^2$ at 750 °C. Furthermore, the PLNGC cathode shows an excellent CO$_2$ resistance in the operation temperature range. The maximum power density of the cell is similar to that when the cathode is exposed to air. Furthermore, the cell performance is stable when the CO$_2$ concentrations in the air vary from 0 to 10 vol.% at both 700 and 750 °C. These results indicate that the PLNGC can be a good candidate for CO$_2$ resistance cathode materials of IT-SOFCs based on YSZ electrolyte.

**1. Introduction**

Solid oxide fuel cell (SOFC) has been considered as one of the most promising device for converting chemical energy of fuel to electrical energy for its high energy conversion efficiency, low emission of pollutants and fuel flexibility [1–5]. However, there are many problems when the SOFC is operated at high temperature, such as high cost and undesired reactions between the electrode and electrolyte, which in turn cause electrode densification and polarization and material degradation [6]. Therefore, many researchers focus on the intermediate temperature solid oxide fuel cells (IT-SOFCs) to resolve the problems of high temperature SOFCs (HT-SOFCs) [7–10]. However, as the operation temperature decreases, the cathode overpotential and interfacial resistances between the electrolyte and electrodes also increase, leading to a lower cell performance [11,12]. The improvement of cathode performance is one of the most important issues for the development of IT-SOFCs [13]. One way is to use a composite cathode to increase the triple phase boundaries (TPBs) of the cathode.

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Alternatively, various mixed ionic electron conductors (MIECs), especially perovskite-type oxides were used to improve the cathode performance at intermediate temperature [15–17]. However, the electrocatalytic performance and chemical stability of the perovskite-type oxides can not have a good compromise [18]. It was reported that the perovskite oxides containing alkaline-earth elements as the SOFC cathode were sensitive to CO₂ even with relatively small quantities [19]. For the practical applications of SOFC, it’s necessary to develop a new cathode with an excellent CO₂ resistance.

Recently, the MIEC with the K₂NiF₄-type structure has received much attention as the potential cathode for the IT-SOFCs [20–27]. The MIEC with the K₂NiF₄-type structure can accommodate a wide range of oxygen stoichiometry that can be modified by slight changes on the composition or oxidation–reduction treatments [28]. Compared with traditional perovskite materials, the MIEC with the K₂NiF₄-type structure possesses better thermal stability, higher surface oxygen exchange coefficients as well as comparable thermal expansion coefficients to the SOFC electrolytes [29]. Recently, Yashima et al. [30] found that a K₂NiF₄-type MIEC material based on Pr₁.₈La₀.₂Ni₀.₇₄Cu₀.₂₁Ga₀.₀₅O₄ (PLNGC) exhibited a significant electronic conductivity. They also reported that the oxygen permeation rate of PLNGC swept by He was quite high in comparison with the conventional ABO₃ perovskite-type MIECs and the PLNGC can be utilized as materials for oxygen separation membranes and cathodes of SOFCs [30]. In our previous work, we found that the PLNGC membrane could even exhibit high oxygen permeation fluxes swept by CO₂, which indicated its excellent performance of CO₂ resistance [31–33]. In this work, the electrochemical properties of PLNGC cathode materials based on YSZ electrolyte are studied. Special attention is paid to the cell performance under the CO₂-containing atmosphere.

2. Experimental

The sol–gel route based on citric acid and EDTA as complexing and gelation agents has been adapted to prepare the Pr₁.₈La₀.₂Nₐ₀.₇₄Cu₀.₂₁Ga₀.₀₅O₄ (PLNGC) powder. Metal Ga was dissolved in nitric acid firstly to form Ga(NO₃)₃ solution. Then stoichiometry amounts of Pr(NO₃)₃, 6H₂O, La(NO₃)₃, 6H₂O, Ni(NO₃)₂, 6H₂O and Cu(NO₃)₂·3H₂O were dissolved in the previous Ga(NO₃)₃ solution followed by the addition of ethylene diamine tetraacetic acid (EDTA), citric acid and NH₃·H₂O. The mixture was then evaporated at 150 °C under constant stirring to obtain a dark green gel. Afterward, the gel was ignited to flame to get the precursor. The precursor was ground and calcined at temperatures up to 950 °C with a heating rate of 2 °C min⁻¹ for 10 h.

The anode precursor hollow fibers were fabricated using wet spinning/phase inversion followed by sintering, as shown in our previous work [34,35]. After drying in air at room temperature, the NiO–YSZ hollow fiber precursors were sintered in static air atmosphere, at 1250 °C for 2 h to form the hollow fibers. The YSZ electrolyte films were deposited onto the anode hollow fibers by dip-coating. The PLNGC cathode was coated on the YSZ electrolyte via brush painting, followed by sintered at 850 °C for 2 h to form the anode-supported hollow fiber SOFC.

The micrographs of the hollow fiber SOFC was observed by the scanning electron microscopy (SEM, S-3700N, Japan). The crystal structures of the powders were characterized by X-ray diffraction (XRD, Rigaku DMax-RR) using Cu-Kα radiation (λ = 0.15404 nm). Continuous scan mode was used to collect 2θ data from 20° to 80° with a 2° min⁻¹ scanning rate. The electric conductivities of the PLNGC sample at different atmospheres were measured by the potentiostatic window of an electrochemical workstation (Zahner IM6ex, Germany). For the conductivity measurements, the PLNGC samples were heated in a tubular furnace from 100 °C to 800 °C with heating rate of 5 °C min⁻¹ in different atmospheres, and the electric conductivity was measured using a DC two-probe method. The gas flow rates were controlled by mass flow controllers (MFC, Bronkhost, Netherland). The cell performance was tested by an Arbin System (BT 2000, USA). The electrochemical impedance spectroscopy was performed by the electrochemical workstation (Zahner IM6ex, Germany) under open-circuit conditions over a frequency range from 0.1 Hz to 0.1 MHz and the signal amplitude is 50 mV.

![Fig. 1](image1.png) Schematic of the fixed apparatus of the anode-supported hollow fiber SOFC based on PLNGC cathode.

![Fig. 2](image2.png) XRD patterns of the (a) YSZ powder, (b) PLNGC powder and (c) YSZ + PLNGC powder (weight ratio of 1:1) sintered at 850 °C for 10 h.
The anode-supported hollow fiber SOFC was fixed in an alumina tube in a tubular furnace, as shown in Fig. 1. Silver wires were fixed by a conductive Ag paste to reduce the contact resistance between the silver wires and the electrodes. Before the electrochemical test, pure hydrogen with a flow rate of 20 ml min\(^{-1}\) was supplied into the core side of the hollow fiber SOFC at 600 °C for 5 h to reduce NiO to Ni. Then moist hydrogen (3 vol.% H\(_2\)O) with a flow rate of 20 ml min\(^{-1}\) was fed into the core side of the hollow fiber SOFC.

3. Results and discussion

Fig. 2 shows the XRD patterns of the YSZ powder, PLNCG powder and YSZ + PLNCG (1:1, w/w) powder sintered at 850 °C for 10 h, respectively. As shown in Fig. 2, the K\(_2\)NiF\(_4\)-type structure was formed when the PLNCG precursor was calcined at 950 °C for 10 h. The PLNCG has a tetragonal I\(_4/mmm\) K\(_2\)NiF\(_4\)-type structure which consists of a (Pr\(_{0.9}\)La\(_{0.1}\))(Ni\(_{0.74}\)Cu\(_{0.21}\)Ga\(_{0.05}\))O\(_3\) perovskite unit and a (Pr\(_{0.9}\)La\(_{0.1}\))O rock salt unit in the whole temperature range (in air between 27 °C and 1015.6 °C) [30]. In order to study the chemical compatibility of the PLNCG and the YSZ, a mixed powder of 50 wt.% PLNCG and 50 wt.% YSZ was calcined at 850 °C for 10 h, then the XRD patterns of the mixed powder were measured. As shown in Fig. 2, no new phases except for the PLNCG and the YSZ were observed, which revealed the good chemical compatibility of the PLNCG and the YSZ at high temperatures.

Fig. 3 presents the SEM images of the anode hollow fiber support. In Fig. 3(a), the anode hollow fiber sintered at 1250 °C for 2 h has an outer diameter and inner diameter of about 0.9 and 0.6 mm, respectively. It can be seen that the anode hollow fiber has an asymmetric structure with a finger-like structure at the inner side and a sponge-like structure at the outer side.

Fig. 4 – SEM images of the cell NiO–YSZ/YSZ/PLNCG, (a) the cross section of the cell, (b) the interface of PLNCG cathode and YSZ electrolyte, (c) the outer surface of YSZ electrolyte, (d) the outer surface of PLNCG cathode.
as shown in Fig. 3(b). The finger-like structure can provide the diffusion and delivery channels for H2. The sponge-like layer near the YSZ electrolyte layer can provide the catalysis area for the oxidation of H2 and enlarge the anode triple phase boundary (TPB).

Fig. 4 presents the SEM images of the NiO–YSZ/YSZ/PLNCG cell. In Fig. 4(a), the YSZ electrolyte is gastight and connected tightly with the NiO–YSZ anode and the PLNCG cathode. The thickness of the YSZ electrolyte layer is about 12 μm. Fig. 4(c) shows the outer surface of the YSZ electrolyte. It can be seen that the YSZ layer is composed of irregular grains without any cracks. The outer surface of the PLNCG cathode is shown in Fig. 4(d). The PLNCG cathode prepared by brush painting is porous.

Fig. 5 shows the electric conductivities of the PLNCG between 100 and 800 °C in O2, air, N2 and CO2. The total electrical conductivity of the PLNCG increases with increasing temperature between 100 °C and about 460 °C, which indicates a semiconducting behavior; then the total electrical conductivity decreases with increasing temperature when the temperature is higher than 460 °C, indicating a metallic nature. The maximum electric conductivity of the PLNCG was 32 S cm⁻¹ in air and 34 S cm⁻¹ in O2, respectively. The maximum electric conductivity of PLNCG appeared at about 460 °C. The maximum electric conductivity of PLNCG is in agreement with the value reported by Yashima et al. [30]. The total conductivity increases with increasing the oxygen partial pressure, which indicates the p-type conduction and the formation of electronic holes [30]. The charge carriers of the PLNCG oxides are electronic holes and oxygen ions.

Fig. 6 – I–V–P curves of the anode-supported hollow fiber SOFC based on PLNCG cathode tested at different temperatures, with 20 ml min⁻¹ H2 (3 vol.% H2O) as fuel and ambient air as oxidant.

Fig. 7 – Electrochemical impedance spectroscopy of the anode-supported hollow fiber SOFC based on PLNCG cathode measured under open-circuit voltage, with 20 ml min⁻¹ H2 (3 vol.% H2O) as fuel and ambient air as oxidant at different temperatures. Inset in Fig. 7 shows an expanded view of the bottom left hand portion of Fig. 7.

Fig. 8 – Ohmic resistances, polarization resistances and total resistances obtained from the electrochemical impedance spectroscopy of the anode-supported hollow fiber SOFC based on PLNCG cathode tested at 600–750 °C under open-circuit voltage condition.
Considering the very low mobility of oxygen ions compared to that of electrons, the measured total electrical conductivity is mainly come from the electronic conductivity. The dominant electronic hole conduction may come from the formation of higher valence number of Pr (Pr^{3+}/Pr^{4+}) or Ni (Ni^{3+}/Ni^{4+}) in perovskite layers [36]. Furthermore, the conductivities in N_{2} and CO_{2} atmospheres between the operation temperature of SOFC (450–800 °C) was similar, implied that CO_{2} had no influence on the electrical conductivity of the PLNCG like N_{2}. Furthermore, it was found that the PLNCG had good phase stability even in pure CO_{2} between room temperature and 1000 °C in our previous work [31]. After around 700 °C, the electrical conductivity decreases slightly with the increasing temperature, which could be due to the equilibration of the dominant electronic hole conduction coming from the formation of higher valence number of Pr (Pr^{3+}/Pr^{4+}) or Ni (Ni^{3+}/Ni^{4+}) in perovskite layers.

Fig. 6 shows the I–V–P curves of the hollow fiber SOFC based on the PLNCG cathode sintered at 850 °C for 2 h. The hollow fiber SOFC with the PLNCG cathode yielded peak power densities of 125, 350, 506 and 876 mW cm^{-2} at 600, 650, 700 and 750 °C, respectively. The results were better than that of the anode-supported hollow fiber SOFC with LSM material as the cathode reported by Yang et al. [37]. It is believed that the improved cathode property is due to the extended reaction sites from the triple-phase boundary (TPB) in pure electron conductor to the whole cathode surface in MIEC, consequently enhances the cell performance when a MIEC is used as the cathode [22]. The OCV is 1.117 V at 600 °C and decreases with increasing temperature (1.084 V at 750 °C). The value of OCV could be calculated by the following formula:

\[
E = E^\circ + \frac{RT}{F} \ln \frac{P_{H_2}P_{O_2}}{P_{H_2O}}
\]

E and \(E^\circ\) are the electromotive force (V) and the standard electromotive force (V) of the SOFC, respectively. R, T and F are the molar gas constant (8.314 J mol^{-1} K^{-1}), temperature (K) and Faraday’s constant (96,485 C mol^{-1}), respectively. \(P_{O_2}\), \(P_{H_2}\) and \(P_{H_2O}\) are the partial pressures of \(O_2\), \(H_2\) and \(H_2O\), respectively. All the OCVs are close to the theoretical values. It indicates the gastightness of the YSZ electrolyte.

The electrochemical impedance spectroscopy (EIS) of the hollow fiber SOFC based on the PLNCG cathode is shown in Fig. 7. The high frequency intercept at the real axis represents the ohmic resistance of the hollow fiber SOFC. It includes the oxygen ion conductivity of the YSZ electrolyte, the electron conductivity of the electrodes, and the contact resistance associated with the interfaces. The low frequency intercept...
at the real axis corresponds to the total resistance of the hollow fiber SOFC. The difference between the low frequency intercept and the high frequency intercept in the real axis is the polarization resistance. The ohmic resistances for the cell are 0.44, 0.18, 0.11, 0.08 $\Omega \text{cm}^2$ at 600, 650, 700, 750 °C, respectively; the total resistances are 3.73, 1.39, 0.91, 0.49 $\Omega \text{cm}^2$ at 600, 650, 700, 750 °C, respectively. The ohmic, polarization and total resistances of the cell at different temperatures obtained from the EIS test are summarized in Fig. 8. Both the ohmic and polarization resistances decrease with increasing temperature. The decrease of the ohmic resistance results from the increase of the oxygen ion conductivity of the electrolyte at elevated temperature. Simultaneously, the decrease of the polarization resistance is attributed to the enhanced kinetics of the electrodes at increasing temperature.

As reported by Yan et al. [19], the perovskite oxide Ba$_0.5$Sr$_0.5$Co$_0.8$Fe$_0.2$O$_3$-$\delta$ which contains alkaline-earth elements as the cathode for SOFC was sensitive to CO$_2$ even with relatively small quantities (0.28–3.07 vol.%) at the range of 600–750 °C. The effects of CO$_2$ on La$_0.6$Sr$_0.4$CoO$_3$-$\delta$ (LSC) and La$_0.8$Sr$_0.2$MnO$_3$-$\delta$ (LSM) cathode were also investigated by Zhao et al. [38]. The presence of CO$_2$ in O$_2$ flow leads to a decrease in ohmic, polarization and total resistances of the cell at different CO$_2$ concentration respectively. The ohmic, polarization and total resistances successively changed to 0, 0.03, 5 and 10 vol.% on the cathode atmosphere with the CO$_2$ concentration varied from 0 to 10 vol.%. These results demonstrate that the PLNCG could be a good candidate for CO$_2$ resistance cathode materials of IT-SOFCs.

4. Conclusion

The K$_2$NiF$_4$-type oxide Pr$_{1.8}$La$_{0.2}$Ni$_{0.74}$Cu$_{0.21}$Ga$_{0.05}$O$_4$ (PLNCG) prepared by sol–gel method has been investigated as a CO$_2$ resistance cathode material for the potential application in IT-SOFC. The PLNCG had good chemical compatibility with YSZ. The electric conductivities of the PLNCG were 30–27 S cm$^{-1}$ between 600 and 750 °C in air. For the anode-supported hollow fiber SOFC NiO–YSZ/YSZ/PLNCG, the maximum power density is 876 mW cm$^{-2}$ and the polarization resistance is 0.41 $\Omega \text{cm}^2$ at 750 °C. The PLNCG cathode shows a good CO$_2$ resistance at the intermediate operation temperature range of SOFC. These results indicate that the PLNCG could be a good candidate for CO$_2$ resistance cathode materials of IT-SOFCs.

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